NEW HYDROCARBON STABILISERS FOR DISPERSION POLYMERISATION IN SUPERCRITICAL CARBON DIOXIDE

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Declaration

Except where specific reference has been made to other sources, the work presented in this thesis is the original work of the author. It has not been submitted, in whole, or in part, for any other degree or professional qualification.

Signed..... Date...13/6/2012

Natasha Birkin

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Abstract

This thesis details the synthesis of highly CO_2-soluble hydrocarbon stabilisers using reversible addition fragmentation chain transfer (RAFT) polymerisation techniques, and their application in the dispersion polymerisation of *N*-vinyl pyrrolidone (NVP) in supercritical carbon dioxide ($scCO_2$).

Chapter 1 outlines the key themes explored throughout the thesis. This introductory chapter focuses on the RAFT polymerisation process, the use of $scCO_2$ as an alternative solvent for polymerisation, and the process of dispersion polymerisation, including the types of stabilisers employed in such reactions.

In Chapter 2, the equipment and characterisation techniques are detailed. The high pressure vessels used extensively throughout the thesis are described, including the high pressure variable volume view cell and the 60 ml clamp-sealed autoclave. Polymer characterisation techniques such as scanning electron microscopy (SEM), nuclear magnetic resonance (NMR) and gel permeation chromatography (GPC) are also considered.

Chapter 3 is the first of three research chapters, and investigates the synthesis of hydrocarbon stabilisers composed of the monomers of vinyl acetate (VAc) and vinyl pivalate (VPi) using xanthate-mediated RAFT polymerisation. The phase behaviour of a range of stabilisers in $scCO_2$ is determined through cloud point measurements using a high pressure variable volume view cell. The impact of adjustments to parameters such as polymer composition and molecular weight on CO_2-solubility are considered.

Chapter 4 details the application of the homopolymers and statistical copolymers of VAc and VPi synthesised in the previous chapter. The polymers are employed as stabilisers in the dispersion polymerisation of NVP in $scCO_2$. A range of stabilisers are considered and the resulting poly(vinyl pyrrolidone) (PNVP) products compared using NMR and SEM to gauge the effect on particle morphology.

Chapter 5 describes the extension of the research to consider the impact of changes to the hydrocarbon stabiliser architecture. A series of block copolymer structures are prepared, and the phase behaviour and stabilising ability of these materials in $scCO_2$ is considered. Additionally, modification of the α- and ω-end of the RAFT-terminated polymers is considered through use of a different xanthate-based RAFT agent, and modification of the polymer post-polymerisation *via* radical-induced reduction.

Chapter 6 describes the overall conclusions obtained from the work presented in the thesis, and also details possible avenues for further research in this area.

Abbreviations and Acronyms

AIBN	Azobisisobutyronitrile
AM	Acrylamide
AN	Acrylonitrile
ATRP	Atom Transfer Radical Polymerisation
CRP	Controlled Radical Polymerisation
C_v	Coefficient of Variance
DMAEMA	Dimethyl Amino Ethyl Methacrylate
DPAEMA	Dipropyl Amino Ethyl Methacrylate
D_n	Average Particle Size Diameter
DSC	Differential Scanning Calorimetry
D_p	Degree of Polymerisation
GPC	Gel Permeation Chromatography
J_{crit}	Critical Chain Length
K	Kg/Mol
MADIX	Macromolecular Design via the Interchange of Xanthates
NMP	Nitroxide-Mediated Polymerisation
NVP	*N*-Vinyl pyrrolidone
NMR	Nuclear Magnetic Resonance
MA	Methyl Acrylate
MMA	Methyl Methacrylate

M_w	Weight average Molecular Mass
M_n	Number Average Molecular Mass
P_c	Critical Pressure
PDI	Polydispersity Index
PDMS-mMA	Poly(Dimethyl Siloxane) Mono Methacrylate
PFOA	Poly(1,1-Dihydroperfluoroctyl Acrylate)
PFOMA	Poly(1,1-Dihydroperfluoroctyl Methacrylate)
PFOEMA	Poly(1,1-Dihydroperfluoroctylethylene Methacrylate)
PFPO	Poly(Perfluoroproylene Oxide)
PMMA	Poly(Methyl Methacrylate)
PNVP	Poly(Vinyl Pyrrolidone)
PPG	Poly(Propylene Glycol)
PS	Poly(Styrene)
PVAc	Poly(Vinyl Acetate)
PVBu	Poly(Vinyl Butyrate)
PVOc	Poly(Vinyl Octanoate)
PVPi	Poly(Vinyl Pivalate)
R	Free Radical Leaving Group on RAFT Agent
RI	Refractive Index
RAFT	Reversible Addition-Fragmentation Chain Transfer
$scCO_2$	Supercritical Carbon Dioxide
SCF	Supercritical Fluid
SEM	Scanning Electron Microscopy

SiMA	3-[Tris(Trimethylsilyloxy)Silyl]Propyl Methacrylate
T_c	Critical Temperature
T_g	Glass Transition Temperature
VAc	Vinyl Acetate
VBu	Vinyl Butyrate
VOc	Vinyl Octanoate
VPi	Vinyl Pivalate
VnDc	Vinyl *neo*-Decanoate
V-70	2,2'-Azobis (4-Methoxy-2,4-Dimethylvaleronitrile)
Z	Stabilising Group on RAFT Agent

Thesis Contents

Chapter 1: Introduction

This chapter aims to provide a more in-depth background for the underlying themes present throughout this thesis. The chapter focuses on the fundamental aspects of polymer chemistry and the general synthetic procedures, including controlled polymerisation techniques, with a focus on RAFT/MADIX polymerisation. The chapter also examines the use of supercritical fluids, in relation to supercritical carbon dioxide, and the application of $scCO_2$ as a clean, green alternative to conventional solvents in polymer synthesis.

1.1 Polymer Chemistry

1.1.1 Introduction to Polymers

A polymer may be defined as a large macromolecule composed of repeating smaller structural units known as monomers, joined together by covalent chemical bonds.[1] The long chains of monomers that would usually constitute a polymer are arranged linearly, and thus tend to adopt long, flexible configurations.

Polymers occur naturally in many forms; cellulose in the cell walls of plants, natural rubber obtained predominantly from the *Hevea Brasiliensis* tree, and deoxyribonucleic acid (DNA) are just a few well-known examples.[2] In addition to natural polymers, the development of synthetic polymers such as poly(ethylene) and nylon have formed the basis of a massively expanding polymer industry.[3] Such polymers exhibit a vast range of physical and chemical properties, making them versatile materials for widespread use in numerous applications.[4] Polymers are employed as adhesives, coatings, lubricants and in packaging.[5] Also, polymers have found a variety of uses in the medical industry, from implants to drug delivery devices.[6, 7] Subsequently, polymeric materials have become an essential component of modern day life.

Polymers exist in a number of forms and the use of different combinations of monomers will result in a variation in the polymer structure produced. The distribution of the monomer repeat units in the polymer backbone is generally used to classify the type of copolymer structure. A variety of different copolymer structures exist (Figure 1.1).[8]

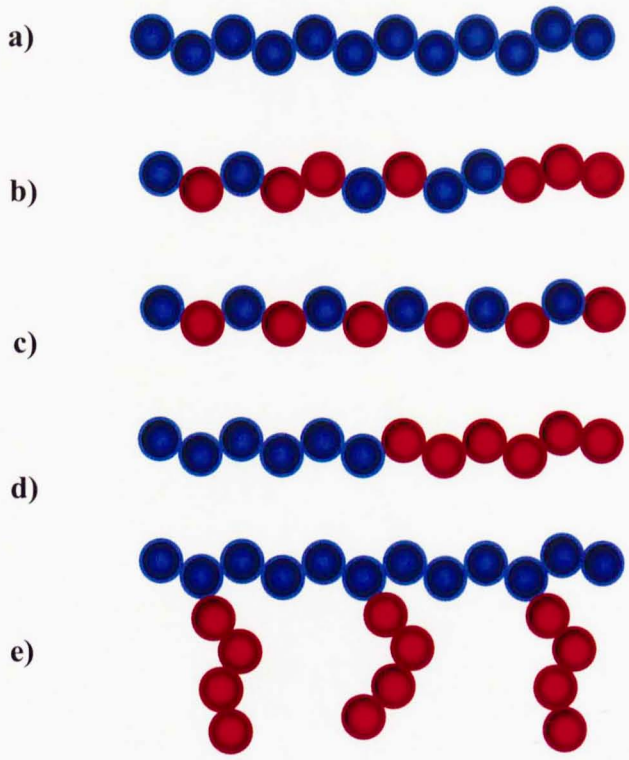


Figure 1.1: Typical polymer structures adopted from the combination of two monomer units where monomer A = ● and monomer B = ● ; a) homopolymer; b) statistical copolymer; c) alternating copolymer; d) block copolymer; e) graft copolymer.

A linear polymer is produced from the polymerisation of one single type of monomer and is referred to as a homopolymer (Figure 1.1, a). However, when a polymer is derived from more than one monomeric species, a copolymer structure is formed.[9] The type of copolymer produced will be dependent upon the concentration and reactivity ratios of each respective monomer employed.[10] A statistical copolymer involves a repeat unit distribution which obeys known statistical laws (Figure 1.1, b). A random copolymer is a statistical copolymer

which has a completely random distribution of monomer units in the polymer structure. Alternating copolymers have a structural backbone arrangement of alternating A and B monomer units (Figure 1.1, c). Block copolymers are formed *via* sequential polymerisation of one monomer, followed by the introduction of a second monomer (Figure 1.1, d). This results in a polymer composed of two or more chemically distinct homopolymer subunits which are covalently linked to one another. Finally, a graft copolymer is composed of a polymer backbone of monomer unit A, which has polymeric side chains attached to it composed of monomer B (Figure 1.1, e). Both block and graft copolymers will possess the characteristics of both components, whereas statistical, random and alternating structures will have intermediate properties of each of the monomer types.

Polymeric materials may be produced using two main methods referred to as step growth polymerisation and chain growth polymerisation.

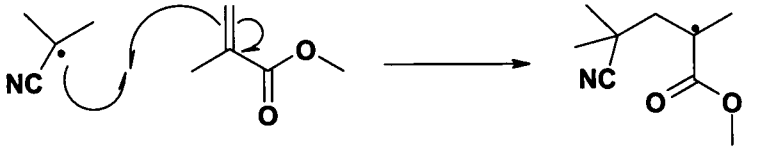
Step growth polymerisation involves the stepwise intermolecular addition of functional monomer molecules to a growing polymer chain. Polymer chain growth most commonly involves an intermolecular condensation reaction between related functional groups (-OH, -COOH, $-NH_2$, -NCO) in successive steps.[11] This is usually accompanied by the elimination of a small molecule such as H_2O for each addition of a monomer unit.[12] Monomers employed in step growth polymerisation also tend to have two reactive functional groups. The molecular weight will increase at a very slow rate until a high conversion is reached (typically >95%).[13]

Chain growth polymerisation, also known as addition polymerisation, involves the formation of a polymer chain through repeat addition reactions with the monomer unit(s). Typically chain growth polymerisation involves unsaturated vinyl monomers, generally in the form of a π double bond.[13] These enable the generation of reactive centres, usually in the form of free radicals, but also anionic/cationic species and organometallic complexes.[2] Chain growth polymerisation involves three main steps; initiation, propagation and termination. Free radical polymerisation is the most commonly employed chain polymerisation technique.[14]

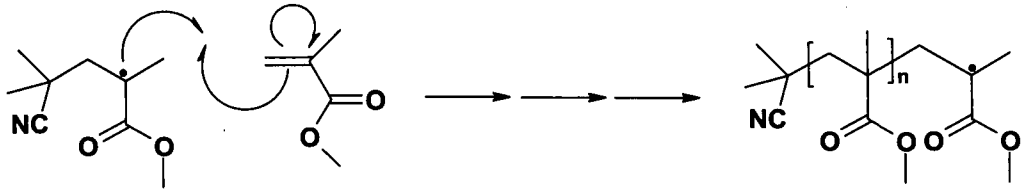
1.1.2 Free Radical Polymerisation

Free radical polymerisation is a widely employed technique, owing to its versatility and synthetic ease. This method of polymerisation is one of the most commonly adopted because it is tolerant to a broad range of monomers with a variety of functional groups.[14] The technique is suitable for different polymerisation conditions including bulk, solution, suspension and emulsion polymerisations. Polymerisations can also be conducted in a range of different solvents, such as aqueous media,[15] organic solvents, ionic liquids[16] and supercritical fluids.[17] A tolerance to water and protic solvents is a key advantage of free radical polymerisation, allowing the development of emulsion and suspension techniques.[14] The process of free radical polymerisation consists of three key steps; initiation, propagation and termination (Figure 1.2).

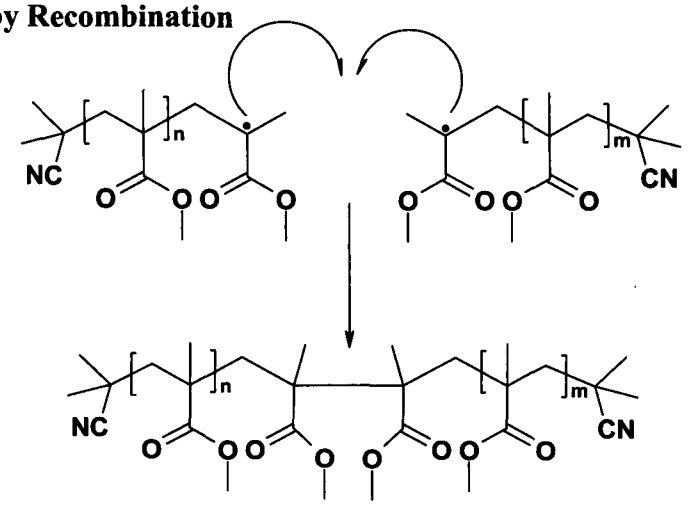
a) Initiation



b) Propagation



c) Termination by Recombination



d) Termination by Disproportionation

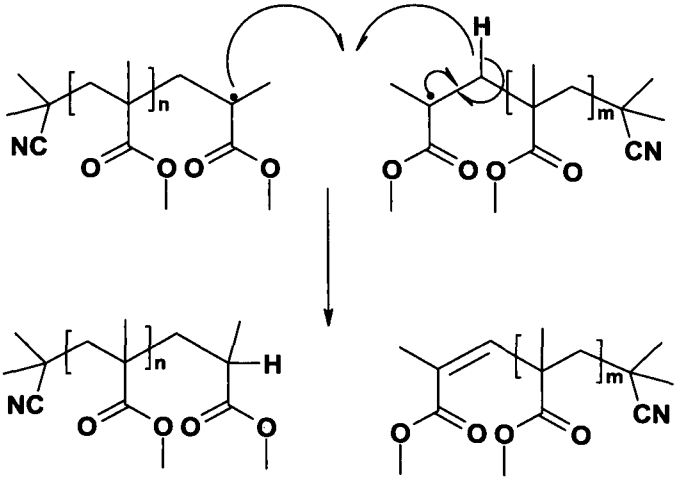


Figure 1.2: Typical free radical polymerisation of MMA.[8]

Initiation involves the production of a free radical *via* an initiator, which will subsequently enable production of a monomer radical. For unsaturated monomers this involves the free radical opening the π bond to form a new radical. Upon activation of the double bond, the monomer opens up to form two single σ bonds (Figure 1.2, a).

Initiators are essential for the generation of free radicals during the polymerisation process, ideally under mild conditions. Most initiators, such as peroxides, tend to possess weak bonds, with small bond dissociation energies, leading to facile dissociation and the production of radical species, able to promote radical reactions. Several methods of radical formation can be employed, although thermal decomposition is the most widely adopted.[14] There are a number of initiators available, such as azo and peroxide compounds which will readily undergo homolytic bond cleavage to form radicals.

The time for the concentration of initiator to decrease to one half of its original concentration is called the initiator half-life ($t_{1/2}$). The initiator species 2, 2'-azobis(isobutyronitrile) (AIBN) is widely employed in this thesis as it will decompose at relatively low temperatures and has a half-life of 4.8 hours at 70 °C (Figure 1.3).[8, 18] The facile dissociation of azo compounds is not due to the presence of a weak bond as is the case for the peroxide compounds. The driving force for the dissociation of azo initiators, including AIBN, is the production of a highly stable nitrogen molecule in addition to the formation of two isobutyronitrile radicals.[8]

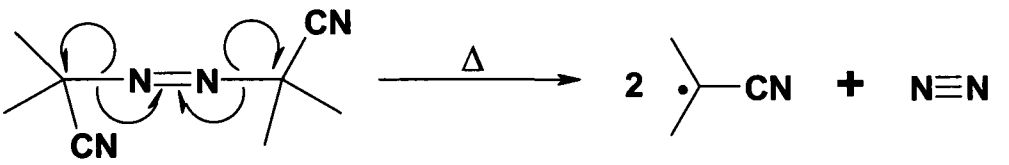


Figure 1.3: Thermal decomposition of AIBN resulting in the formation of isobutyronitrile radicals for the initiation of a free radical polymerisation process. Decomposition occurs through homolytic cleavage and is driven by the production of N_2.

Propagation involves growth of the monomer radical *via* reaction with other monomers within the system, transferring the free radical to the end monomer unit and involving successive propagation of the reactive centre (Figure 1.2, b).[19] The propagating radical can potentially attack either end of the vinyl double bond of the monomer.[20, 21] Head-to-tail addition is the most favourable arrangement, and involves the least substituted end. The head is defined as the most substituted end of the vinyl bond, or the end with the best radial stabilising substituent. Head-to-head addition can also take place, and is defined as attack of the double bond at the most substituted end. Addition of the propagating radical to monomer molecules within the system is rapid, and high molecular weight polymer is usually attained at low conversions. Propagation continues until the active centre is destroyed through termination.

Termination involves the destruction of the radical species, which leads to termination of chain growth. The two main termination steps are combination and disproportionation. Combination involves the linkage of two active polymer end groups, resulting in a dead polymer chain (Figure 1.2, c). Termination through disproportionation involves abstraction of a proton from one propagating chain end to another, leading to the production of two different polymer products (Figure 1.2, d).[22]

Chain transfer is an additional type of termination process that can take place. Chain transfer reactions involve transfer of the active site from the propagating polymer chain to a new chain transfer agent species in the system. Such processes act to terminate the existing polymer chain, but transfer the radical to a new species that can continue to initiate polymerisation. The chain transfer agent can be a monomer, solvent or initiator within the system. Chain transfer agents can be utilised to control the molecular weight obtained during polymerisation. One such example is that of mercaptans (RSH), compounds that have a high affinity for hydrogen atom transfer. By employing a mercaptan in the polymerisation process, the radical is transferred from the polymer chain to the mercaptan, combined with the transfer of a proton from the mercaptan to the polymer.[23-26]

One of the major disadvantages of free radical polymerisation is the difficulty in molecular weight control, and the high polydispersity of the chains being formed in the process. The method also allows for no real control over the molecular structure, as free radical polymerisations are susceptible to automatic termination and chain transfer processes. Controlled radical polymerisation is a technique

which has a number of advantages over traditional free radical polymerisations and can provide a means of combating these issues.

1.1.3 Controlled Radical Polymerisation

Controlled/living radical polymerisation can be used to combat the difficulties associated with free radical polymerisation. Controlled polymerisation techniques provide a route to accessing a vast range of polymers with precise molecular weight and tailored architectures.

Living polymerisation is defined as a polymerisation reaction in which chain termination and chain transfer reactions are absent, and the rate of chain initiation greatly exceeds the rate of propagation. This leads to the production of very similar chain lengths, and thus a low polydispersity. However, truly living radical polymerisations cannot be achieved, as in a radical system bimolecular termination cannot be completely eliminated.[27] Thus the term controlled radical polymerisation (CRP) has been employed to differentiate from a true living system in this thesis.

Szwarc first defined living polymerisation as a chain growth process without chain breaking processes. Following this, in order for a polymerisation to be classed as 'living', certain criteria must be met: [14, 21, 27-30]

- Irreversible chain transfer or termination reactions must be absent, or kept to a minimum within the polymerisation system.

- The bond to the end group must be thermally or photochemically labile and able to undergo reversible homolytic reaction under the reaction conditions to regenerate a propagating radical which can continue polymerisation. Polymerisation proceeds until all monomer has been consumed. Further addition of monomer results in continued polymerisation.

In addition to this, a well-controlled polymerisation will exhibit a number of key features: [21, 31]

- The evolution of number average molecular weight (M_n) will follow a linear function of monomer conversion. This requires that all chains are initiated and grow uniformly.

- The concentration of the active propagating species remains constant. A kinetic plot of ($\ln([M_0]/[M])$ *vs.* time should be linear if the reaction is first-order with respect to the monomer.

- A narrow molecular weight distribution will be obtained, providing all chains grow uniformly. The molecular weight distribution for the system will decrease with conversion, providing the rate of initiation is fast in

comparison to the rate of propagation, and there is slow exchange of the active species. This condition allows simultaneous growth of all the polymer chains.

- Following monomer consumption, end-group functionality of the polymer will be preserved, and the active centre of the species retained. This feature enables the polymer chain ends to be reactivated with the introduction of additional monomer. Consequently access to architectures such as block, graft and star copolymers is possible.

Overall, it is evident that there are a number of advantages in using controlled radical polymerisation techniques. It allows narrow molecular weight distributions to be achieved, providing a system by which all chains grow uniformly, and both the molecular weight and the architecture of the final polymer may be controlled.

The general concept of controlled radical polymerisation is to avoid irreversible bimolecular termination reactions that occur as effectively as possible by decreasing the number of growing radical chains. In controlled radical polymerisation methods, an equilibrium exists between the active free radicals and the dormant species. This equilibrium allows the slow but simultaneous growth of all the polymer chains, whilst the radical concentration is still kept low enough to minimise termination steps.[20, 32] The result is a slower reaction rate, but allows for control of the molecular mass. Radicals may either be reversibly

trapped in a deactivation/activation process, or they can be involved in a ''reversible transfer'', degenerative exchange process.[33]

Four main types of controlled radical polymerisation have been developed; Nitroxide-Mediated stable free-radical Polymerisation (NMP),[34] Atom Transfer Radical Polymerisation (ATRP),[35] Reversible Addition–Fragmentation chain-Transfer (RAFT) polymerisation[36] and Macromolecular Design *via* the Interchange of Xanthates (MADIX).[37] ATRP and NMP will be briefly outlined in the following sections. As RAFT/MADIX polymerisation is the technique employed throughout this thesis, the process will be discussed in greater detail in section 1.1.3.3.

1.1.3.1 Nitroxide-Mediated Polymerisation (NMP)

NMP involves the application of a stable nitroxide radical in a reversible deactivation process.[34, 38-40] Nitroxides are efficient radical scavengers and will combine with carbon-centred radicals to form alkoxyamines. The mechanism of control exploits this feature of nitroxides and is achieved through dynamic equilibrium between the dormant alkoxyamine terminated chains and the actively propagating radicals/growing chains (Figure 1.4).[33]

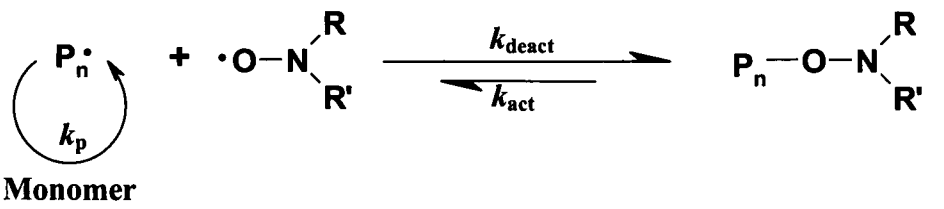


Figure 1.4: General mechanism of Nitroxide-Mediated Polymerisation.

Activation of the dormant species occurs *via* thermally induced homolytic cleavage of the C-O bond of the alkoxyamine, leading to the reversible production of the active chains and the nitroxide radical species.[14] The equilibrium between dormant and active chains is designed to heavily favour the dormant state. The main disadvantages associated with NMP are the severe reaction temperatures required, and the limited range of monomers applicable to the process.

1.1.3.2 Atom Transfer Radical Polymerisation (ATRP)

ATRP is also based on a process of reversible deactivation, and has been widely studied by a number of groups.[35, 41-44] ATRP employs a transition metal species (M), typically copper, coordinated to a suitable ligand (L), forming a transition metal complex (ML_y) which can expand its coordination sphere and increase its oxidation state. In addition, the process requires an alkyl halide (R-X). The transition metal complex undergoes a reversible one electron oxidation step

involving the homolytic cleavage of the alkyl halogen bond, to form a metal halide complex and an organic radical (Figure 1.5).

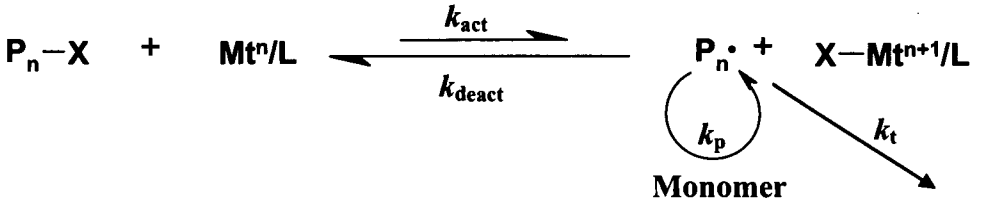


Figure 1.5: General mechanism of ATRP *via* the application of a metal-based catalyst.

The radical will initiate polymerisation with monomer within the system. Propagation occurs until back-transfer of the halogen atom from the transition metal complex to the propagating radical takes place. This results in formation of a dormant species and is known as the deactivation step. A dynamic equilibrium is established in which reversible activation and deactivation reactions rapidly take place, allowing all of the polymer chains in the system to grow at a relatively uniform rate.[45]

1.1.4 RAFT/MADIX Polymerisation

Reversible addition–fragmentation chain-transfer (RAFT) polymerisation is one of the most versatile and robust controlled radical polymerisation techniques. The main advantage of RAFT polymerisation is the wide range of both functional and non-functional monomers it can be used for,[46] and the variety of architectures that can be accessed.[47-53] It also allows polymerisation of monomers in aqueous media at relatively low temperature.[54-56]

Whilst NMP and ATRP are based upon a mechanism of reversible termination, both RAFT and MADIX polymerisation follow a reversible chain transfer mechanism through a stabilised intermediate (Figure 1.6).[46]

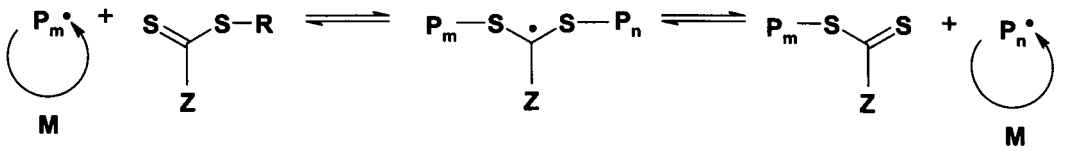


Figure 1.6: General mechanism for RAFT polymerisation, employing a chain transfer agent and involving a reversible chain transfer process.

The mechanism of RAFT/MADIX polymerisation involves initiation, propagation and termination steps as seen commonly in free radical polymerisation. In addition to these steps, there is an important chain transfer step, involving a chain transfer agent (CTA). RAFT and MADIX polymerisation follow the same

mechanism but differ solely on the type of polymerisation mediator employed.[57] MADIX polymerisation is limited to the use of a xanthate compound as a chain transfer agent (CTA), whilst RAFT polymerisation extends to the application of a number of thiocarbonylthio compounds. The term RAFT is often adopted to encompass the MADIX technique.

The CTAs predominantly employed in RAFT processes are thiocarbonylthio species from four main families of compounds, which vary in terms of the Z group substituent; xanthates,[58, 59] dithioesters,[36] dithiocarbamates[60, 61] and trithiocarbonates,[62] the structures of which are shown in Figure 1.7.

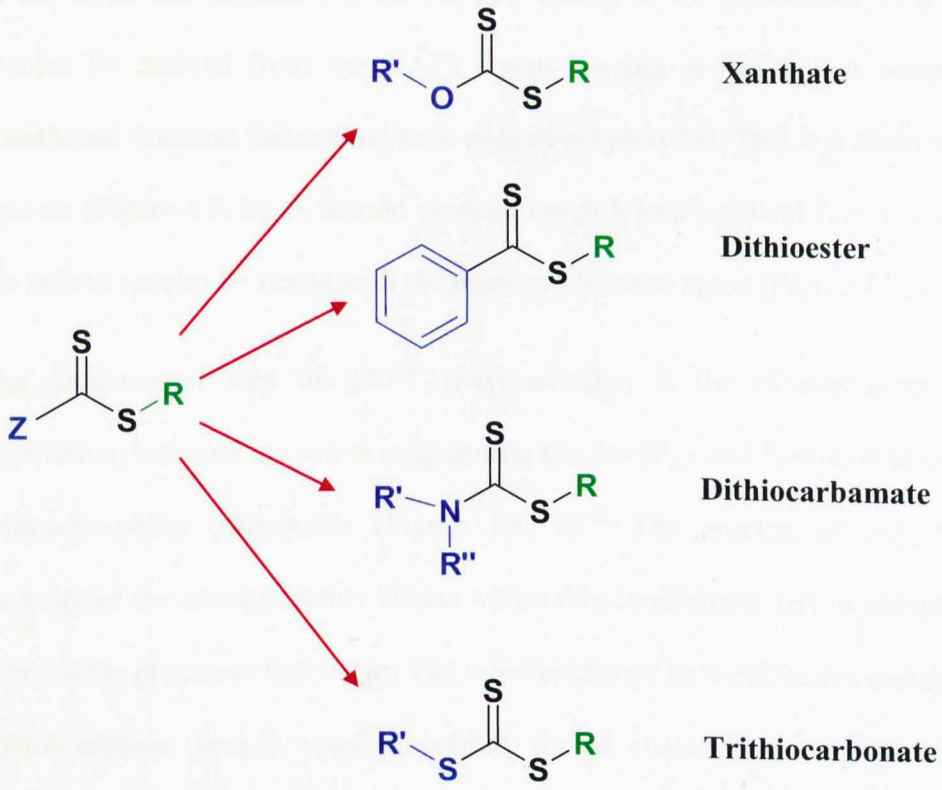


Figure 1.7: Chemical structure of the four main types of thiocarbonylthio RAFT chain transfer agents.

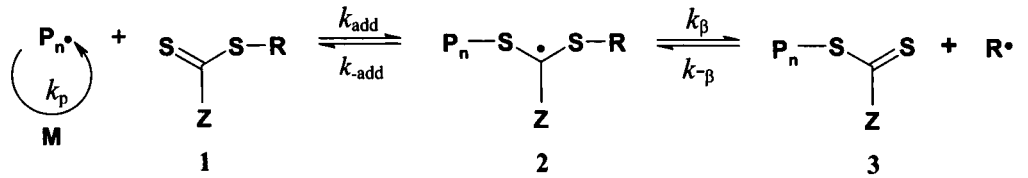
1.1.4.1 The Mechanism of RAFT

In RAFT polymerisation, the activation-deactivation equilibria consist of chain transfer reactions. The full mechanism of RAFT polymerisation is detailed in Figure 1.8.[46, 63, 64] Initiation occurs as with a typical free radical polymerisation. An external source of radicals is required to initiate and maintain polymerisation. The initiator species I• initiates the formation of a propagating radical, P_n• (Figure 1.8, a). After a certain time, addition of the propagating radical to the highly reactive C=S bond of the thiocarbonylthio RAFT chain transfer agent takes place, resulting in the formation of a stabilised intermediate structure (**2**). Fragmentation of the labile intermediate radical occurs, leading to the production of a radical species R• derived from the RAFT agent leaving group, and a temporarily deactivated dormant thiocarbonylthio capped polymer (**3**). This is a chain transfer process (Figure 1.8, b). A second propagating polymeric radical P_m• is formed as the radical species R• reacts with the monomer(s) once again (Figure 1.8, c).

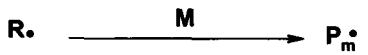
The fundamental step in RAFT polymerisation is the establishment of an equilibrium between the active propagating species (P_m• and P_n•) and the dormant thiocarbonylthio compounds (Figure 1.8, d).[65] The process of trapping the majority of the active polymer chains within this equilibrium acts to minimise the termination processes that occur. The rapid exchange between active and dormant chains ensures there is equal probability for all chains to grow, with minimal terminations, and so the process leads to the production of narrow molecular weight distributions.

a) Initiation

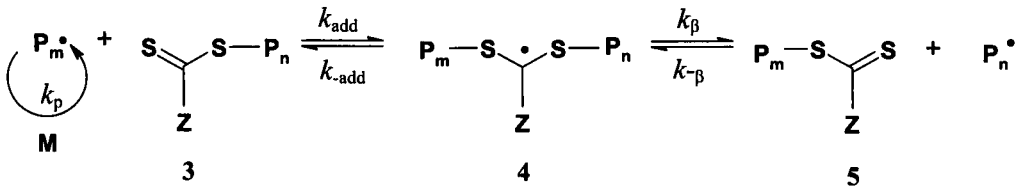
b) Chain Transfer



c) Reinitiation/Propagation



d) Equilibration



e) Termination

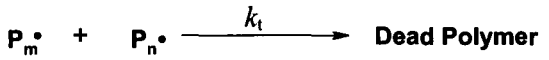


Figure 1.8: Detailed mechanism of RAFT polymerisation: a) Initiation, and the formation of a propagating polymeric radical from an initiator (I) and monomer (M) within the system; b) Chain transfer of the growing polymer chain to the RAFT agent leads to the thiocarbonylthio terminated species and the initiating species R•; c) Reinitiation of polymerisation; d) Chain equilibration between the propagating polymer chains and the dormant RAFT capped polymers, *via* the stabilised intermediate; e) Termination.

The polymer product will be end-capped by the thiocarbonylthio group of the RAFT agent. The R group of the RAFT agent will terminate the other end of the polymer for the majority of chains. Additionally, a small proportion of polymer chains will be capped by the initiator species, although this will typically be negligible as a result of the low concentration of initiator employed in comparison to the RAFT agent.

As with all controlled polymerisation techniques, the RAFT polymerisation process is characterised by a linear increase of the molar mass with respect to monomer concentration. Therefore, the theoretical molecular weight ($M_{n,th}$) can be derived from Equation 1.1, assuming the concentration of the radical initiating species is negligible and the concentration of the RAFT agent and monomer is known.[64]

$$M_{n,th} \approx \frac{[M]_0 - [M]_t}{[RAFT]_0} m_M + m_{RAFT}$$

Equation 1.1: Prediction of theoretical molecular weight ($M_{n,th}$) of polymer synthesised in RAFT polymerisation where $[M]_0$ is the initial concentration of the monomer, $[M]_t$ is the concentration at time t, $[RAFT]_0$ is the initial concentration of the RAFT agent employed, m_M is the molecular weight of the monomer and m_{RAFT} is the molecular weight of the RAFT agent.[64]

In order to obtain a successful RAFT polymerisation that functions ideally, and with living characteristics, a number of conditions need to be met within the system. Initiation should be rapid with respect to propagation, so as to be close to an ideal system in which all chains are initiated simultaneously.[30] Secondly, the number of monomer units added to the active polymeric chain during each active/dormant cycle should be low to allow for a similar rate of chain growth. Also, despite the need for a rapid dormant-active interchange, it is important for the thermodynamic equilibrium to favour the formation of chains in a dormant form. This ensures a low concentration of active propagating radicals is maintained, and helps to minimise bimolecular termination reactions taking place.[57] Additional termination reactions such as chain transfer should also be kept to a minimum.

1.1.4.2 RAFT Agent Structure

Perhaps one of the most important factors that will determine the success of any given RAFT polymerisation process is the choice of RAFT agent structure with respect to the monomer and polymerisation conditions being employed.

The general structure of thiocarbonylthio compounds is S=C(Z)SR, where Z and R may be tailored depending on the properties required (Figure 1.9).[63] When considering the overall structure of the RAFT agent, the key feature is a highly reactive C=S bond (high k_{add}) which is susceptible to radical attack, and is able to combine with the active species.[64, 66] Another important structural feature is the

presence of a weak S-R bond, able to undergo rapid fragmentation and favour the formation of R•, the leaving group radical ($k_{\beta}>k_{-add}$). Z is a group which acts to modify the RAFT agent activity, and R is the free radical leaving group with the ability to reinitiate polymerisation. The nature of the steric and electronic properties of R and Z components within the structure will determine how effective the RAFT chain transfer agent is, and therefore must be considered carefully.

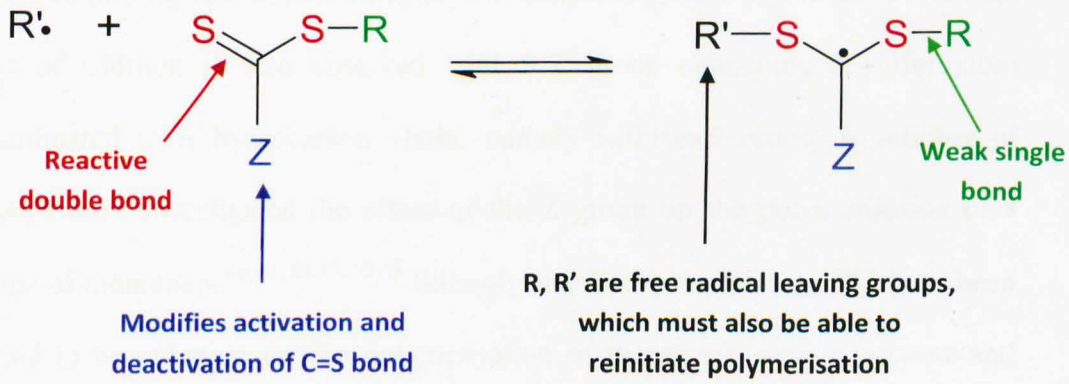


Figure 1.9: Structural features of the RAFT CTA and the corresponding radical intermediate obtained following radical addition.[67] The R and Z group are important variables in the CTA structure and must be chosen with care.

The Z group is known as the activating/stabilising group, and strongly influences the stability of the thiocarbonylthio radical intermediate.[46] Generally, strong

stabilising groups will favour the formation of the intermediate and subsequently enhance the reactivity of the C=S bond towards radical addition.[68, 69] However, if the intermediate radical is too stable, the fragmentation step will be unfavourable, and the reinitiating group R• will not be lost from the RAFT agent. This will result in a greater possibility of intermediate radicals within the system taking place in termination reactions. Therefore, it is important to maintain sufficient fragmentation rates of the intermediate radicals.[68, 70, 71]

A higher rate of addition of radical species to the C=S bond will be observed when employing dithioesters composed of simple alkyl and aryl Z groups. A high rate of addition is also observed with a Z group containing a sulfur atom coordinated to a hydrocarbon chain, namely trithiocarbonates. A number of groups have investigated the effect of the Z group on the polymerisation of a range of monomers.[60, 61, 68, 69, 72-74] Strongly stabilising groups (*e.g.* Ph) have been found to be effective for the polymerisation of monomers such as styrene and methacrylates, because of the high activation of the thiocarbonyl function by the phenyl group.[57]

The situation is rather different when the Z group is weakly stabilising, such as an oxygen or nitrogen atom, in the case of xanthates and dithiocarbamates respectively. In such cases, the non-bonded electron pair on the heteroatom is delocalised with the C=S bond (Figure 1.10).[46, 58] This will lower the double bond character of the C=S bond and consequently lowers the reactivity, making it less susceptible to radical addition (low k_{add}).[75] As a result, the rate of addition to the

sulfur atom is decreased, particularly when using monomers such as bulky methacrylate radicals.[63] This leads to poor control of the growing polymer chains.

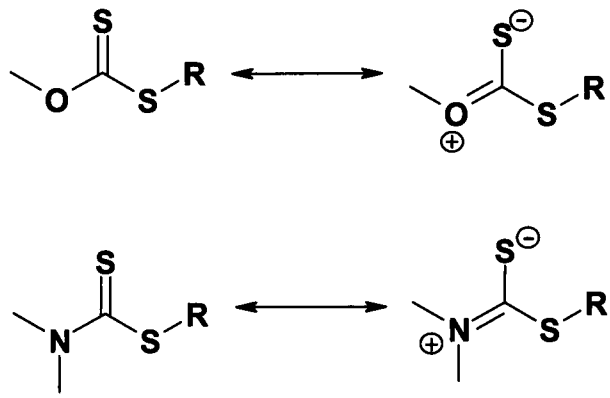


Figure 1.10: Canonical forms of xanthate and dithiocarbonates.

However, O-Alkyl xanthates and N,N-dialkyl dithiocarbamates are specifically suited for the polymerisation of fast propagating vinyl monomers such as VAc and NVP, where the propagating radical is poorly stabilised, and are often employed for the controlled polymerisation of these monomers.[37, 58, 76-79] In the case of such monomers, a C=S bond of lower reactivity is desirable, as it permits the addition of these poorly stabilised propagating radicals to the C=S bond, counterbalancing their instability, and giving some degree of control over the polymer molecular weight.[63]

The R group must possess a good leaving group ability in comparison with the propagating polymer chain, in order to promote fragmentation of the RAFT agent. The R group will also contribute in part towards stabilisation of the radical intermediate, although this is much less significant than the Z group contribution.[63, 80] In addition to an R group substituent that will be a similar or better homolytic leaving group than the propagating radical, steric and electronic factors must also be considered. Sterically bulky R groups will generally be lost from the RAFT agent with greater ease. Electron-withdrawing groups that make the thiocarbonylthio sulfur more electrophilic will also enhance leaving group ability, as does the presence of a radical stabilising component.[80] As with the Z group, choice of R group must be tailored to suit the monomer, providing a balance between an effective homolytic leaving group and a suitable radical for reinitiation.[64, 80-85] One such example is the benzyl group radical $-CH_2Ph$, which is an effective leaving group for the polymerisation of acrylates and styrenics.[62, 80] However, the benzyl R group is a poor leaving group with respect to propagating poly(methyl methacrylate) radicals, and as such, a benzyl R group within the RAFT agent structure is not suitable for MMA polymerisation.[82]

One of the major issues to arise when employing RAFT polymerisation is rate retardation.[63, 86, 87] In such cases, slower polymerisation kinetics are observed in comparison to a conventional free radical polymerisation. Retardation effects generally appear to be much more pronounced in the case of dithiobenzoates.[88-90] Conversely, very little/no retardation has been observed when employing xanthates as chain transfer agents.[58] A number of reasons have been proposed to

explain the observation of rate retardation, including a slow fragmentation of the intermediate radical,[73, 91-93] and side reactions involving termination of the intermediate radical.[94-96] Slow fragmentation occurs as a result of increased stability of the intermediate radicals. The increased stabilisation of dithiobenzoates can be related to the delocalisation of the radicals with the phenyl group, and potentially explains the retardation observed in these systems.[96]

Inhibition is also observed in certain polymerisations, and is the process of slow fragmentation of the intermediate radical at the start of the polymerisation. The effect is enhanced for fast propagating monomers such as VAc. The slow fragmentation arises from the poor homolytic leaving ability of the vinyl acetate radical and the resulting stability of the intermediate radical.

It has been shown that the RAFT agent structure is crucial in obtaining a successful RAFT polymerisation. In view of this, a series of guidelines have been devised for appropriate RAFT agent selection, in order to optimise the RAFT process through the adjustment of the R and Z group, depending on the monomer being polymerised (Figure 1.11).[64, 67]

Full lines indicate a good control over the RAFT polymerisation with the selected monomers, while dashed lines refer to monomer RAFT agent combinations in which only partial control may be achieved. In these cases, there may be broad molecular weight distributions, or substantial retardation/prolonged inhibition.

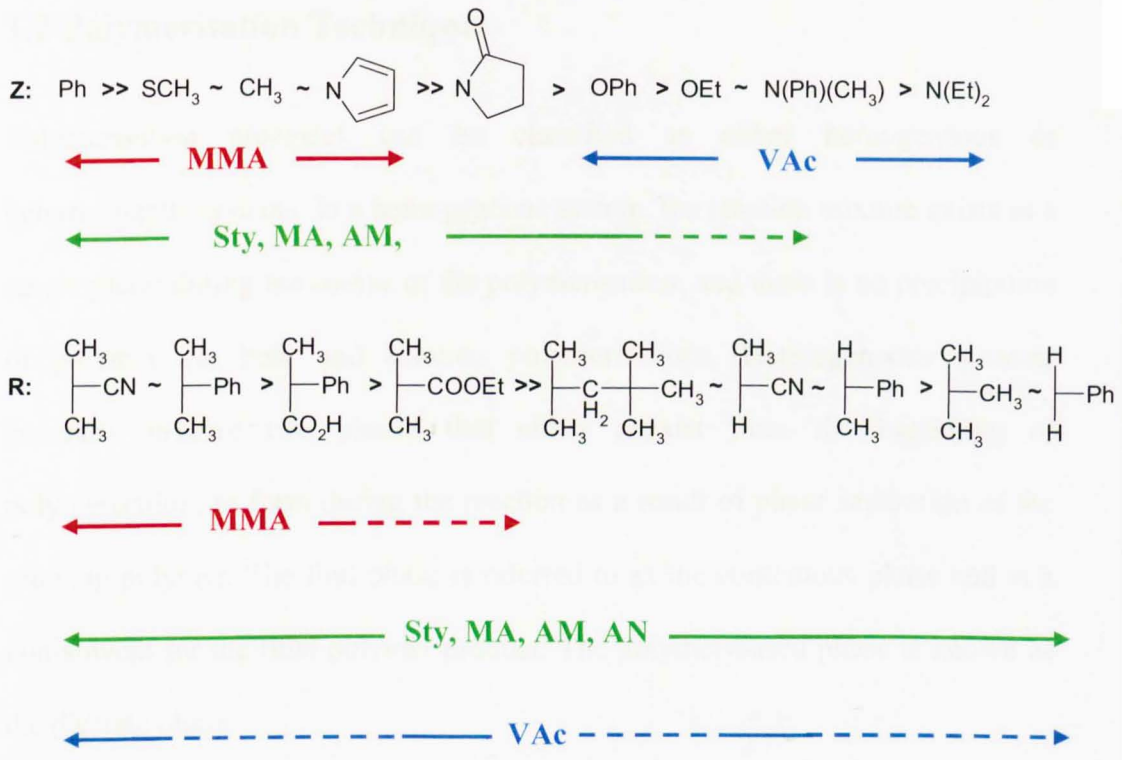


Figure 1.11: Guidelines for RAFT agent selection for typical monomers, where MMA = methyl methacrylate, Sty = styrene, MA = methyl acrylate, AM = acrylamide, AN = acrylonitrile, VAc = vinyl acetate.[64, 67] For 'Z', addition rates and transfer constants decrease and fragmentation rates increase from left to right. For 'R', fragmentation rates decrease from left to right. A straight line indicates good control, while a dashed line denotes limited control.

In this thesis, vinyl esters are predominantly used as the monomers for polymerisation. Therefore, xanthate-mediated RAFT polymerisation will predominantly be employed.

1.2 Polymerisation Techniques

Polymerisation processes can be classified as either homogeneous or heterogeneous systems. In a homogeneous system, the reaction mixture exists as a single phase during the course of the polymerisation, and there is no precipitation of polymer *i.e.* bulk and solution polymerisations. Heterogeneous systems generally involve two phases that either coexist from the beginning of polymerisation, or form during the reaction as a result of phase separation of the growing polymer. The first phase is referred to as the continuous phase and is a non-solvent for the final polymer product. The polymer-based phase is known as the discrete phase.

A range of these polymerisation techniques will be outlined in the following section.

1.2.1 Bulk Polymerisation

Bulk polymerisation involves an initial mixture of a pure monomer, a monomer-soluble initiator, and possible chain transfer agents, leading to a pure polymer product.[8] In bulk polymerisation, no solvent is required because the monomer acts as the solvent system.

The process appears to be a relatively straightforward technique when first considered, but problems regarding heat transfer make it difficult to control, and as such a number of issues exist. During the process, there is an increase in

viscosity as the polymerisation proceeds, which inhibits heat dissipation. This leads to heat transfer and product handling difficulties. Auto-acceleration can also occur, through a process known as the Trommsdorff-Norrish effect, and results in a reduction in the rate of termination, causing further heat production.[97, 98]

The risk of potentially explosive thermal runaway occurring makes bulk polymerisation difficult to carry out in practice. If the technique is used for strongly exothermic addition reactions, the risk of thermal runaway is greater, and so the reactions tend to be stopped at low conversion. This prevents any significant increase in viscosity, and allows the mixture to remain easy to stir. However, the problems associated with bulk polymerisation mean that when employed for controlled radical polymerisation techniques, a lack of control can be observed.

As a result of these disadvantages, bulk polymerisation is not widely employed in industry. Poly(ethylene) and poly(styrene) are two of the few polymers produced *via* the bulk polymerisation technique.[2]

1.2.2 Solution Polymerisation

Solution polymerisation involves a medium in which the monomer is dissolved in a solvent. The presence of solvent ensures that many of the problems associated with bulk polymerisation may be overcome, as the heat and viscosity of the resulting mixture are more efficiently controlled by dilution.[14]

Ideally, the chosen solvent requires low chain transfer activity in order to minimise any potential chain transfer reactions with the solvent molecules occurring.[99] One of the main disadvantages associated with solution polymerisation is the difficulty in removing all traces of solvent from the final polymer product. Therefore, for commercial polymer production, the method only tends to be used if the polymer is required in solution (*i.e.* a lacquer or adhesive).[100] Additionally, the reaction temperature is limited to the boiling point of the solvent used, subsequently restricting the rate of reaction.[2] Solution polymerisation is one of the principal methods used in the production of poly(acrylonitrile).[20]

1.2.3 Precipitation Polymerisation

Precipitation polymerisation is based upon solution polymerisation, but occurs if the resulting polymer product is insoluble in the solvent. The polymerisation is initially homogeneous, but precipitation takes place as the polymer forms. The method allows for easy separation of the final polymer from the solvent, but often the resulting particles are irregular in shape.[14]

1.2.4 Suspension Polymerisation

This polymerisation method involves the suspension of the monomer/initiator reaction mixture as fine droplets in an inert solvent medium, often water.[2, 14]

Water-soluble suspension agents are used as stabilisers, which attach to the surface of the monomer droplets and prevent coalescence. The mixture undergoes continuous controlled mechanical agitation to produce droplets of a relatively uniform size, which all effectively act individually as small scale bulk polymerisation systems. The technique works due to the large number of such micro-droplets undergoing bulk polymerisation, converting the monomer droplets into polymer beads.

The degree of agitation will affect the size of the polymer beads produced.[101] The process allows for easy heat removal and control due to the large surface area of the droplets, and the resulting polymer may be isolated *via* spraying or filtration. However, for polymers which are very soluble in their own monomer, stirring must be extremely vigorous in order to prevent agglomeration.

Suspension polymerisation is industrially employed for the synthesis of polymers such as poly(vinyl chloride).[101]

1.2.5 Emulsion Polymerisation

Emulsion polymerisation is a development of suspension polymerisation, and one of the most widely used techniques. As with suspension polymerisation, the monomer is insoluble in the reaction medium and dispersed as a uniform emulsion.[102] The initiator is soluble in the reaction medium rather than the monomer.

Droplets of the monomer are dispersed in an aqueous medium with the aid of an emulsifying agent, commonly an anionic surfactant (detergent), composed of a hydrophilic head and hydrophobic tail (Figure 1.12).

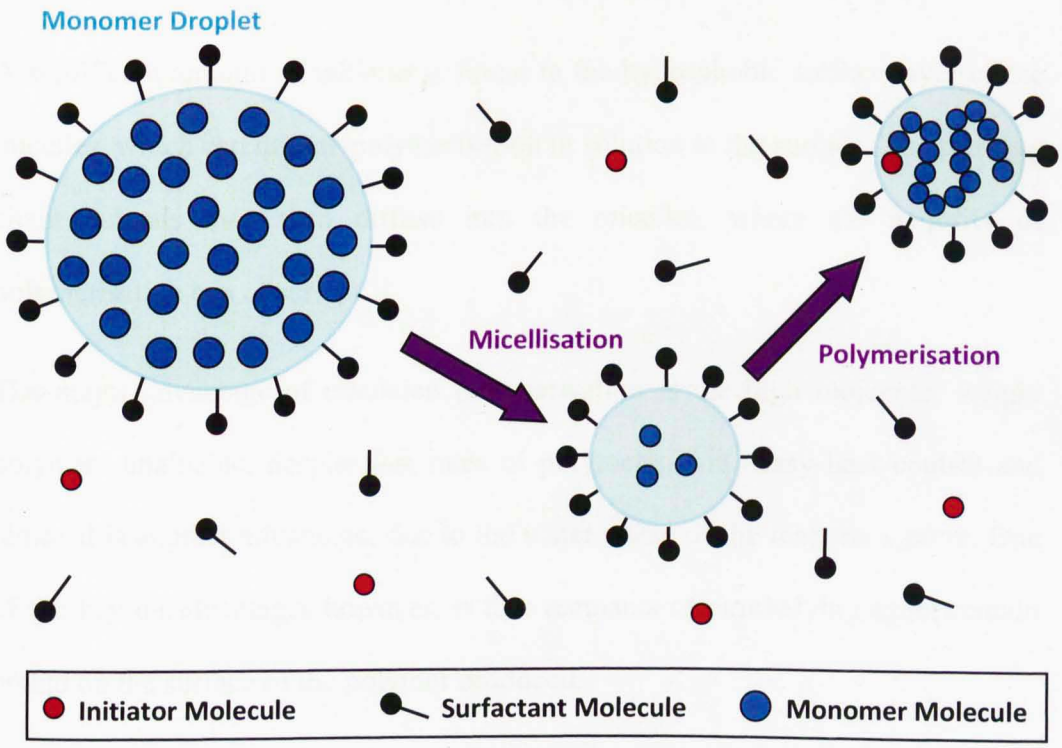


Figure 1.12: Diagram representing a typical emulsion polymerisation. Inititor radicals migrate into stabilised monomer micelles where polymerisation can subsequently take place. Monomer droplets supply additional monomer through migration into the polymerisation medium.

Small detergent micelles are formed which contain a small quantity of the monomer in a solubilised form. In addition, larger droplets of monomer exist which are stabilised by the detergent. No significant polymerisation takes place within the monomer droplet as the initiator is not soluble within it, and the droplets act to feed the reaction medium with monomer.

A significant amount of initiator is found in the hydrophobic surface layer of the micelles, which can initiate polymerisation in solution at the surface. The growing chain radicals may then diffuse into the micelles, where the majority of polymerisation can occur.

The major advantage of emulsion polymerisation is the high molecular weight polymers attainable, despite fast rates of polymerisation. Easy heat control and removal is another advantage, due to the water phase of the reaction system. One of the key disadvantages however, is that remnants of emulsifying agent remain bound on the surface of the polymer produced.

The process of emulsion polymerisation is a widely employed technique, and is responsible for producing the largest volume of paint binders for the coatings industry.[102]

1.2.6 Dispersion Polymerisation

A typical dispersion polymerisation is a modified version of precipitation polymerisation. Initially the system will consist of a homogeneous solution of monomer and initiator, although the overall polymerisation process is heterogeneous as the resulting polymer is insoluble and will precipitate out as a stabilised colloidal dispersion.[103, 104]

A stabiliser, also referred to as a surfactant, is required in dispersion polymerisation techniques in order to form a colloidal dispersion. In the absence of the stabiliser, the polymeric dispersion will be unstable and coagulation of the precipitated polymer particles will occur. In dispersion polymerisation, the precipitated polymer particles are able to form a stable latex because of the presence of the stabiliser molecule, which is anchored onto the surface of the polymer particle and provides a steric stabilisation mechanism.[105] This is a result of the surfactant generating a repulsive force, which keeps the individual growing polymer chains sufficiently far apart, so that attractive Van der Waals interactions between the particles become too weak to allow aggregation to take place. The particles are then free to capture initiator, monomer and radical chains, allowing polymerisation to proceed in the continuous and particle phase.

Dispersion polymerisation involves two main stages; particle nucleation and particle growth.

Polymerisation is initiated in the homogeneous phase and free radicals react with monomer in solution to form oligomeric polymer radicals (Figure 1.13, a). During

the polymerisation, the growing polymer chains reach a certain critical chain length where they are no longer soluble in the continuous phase.

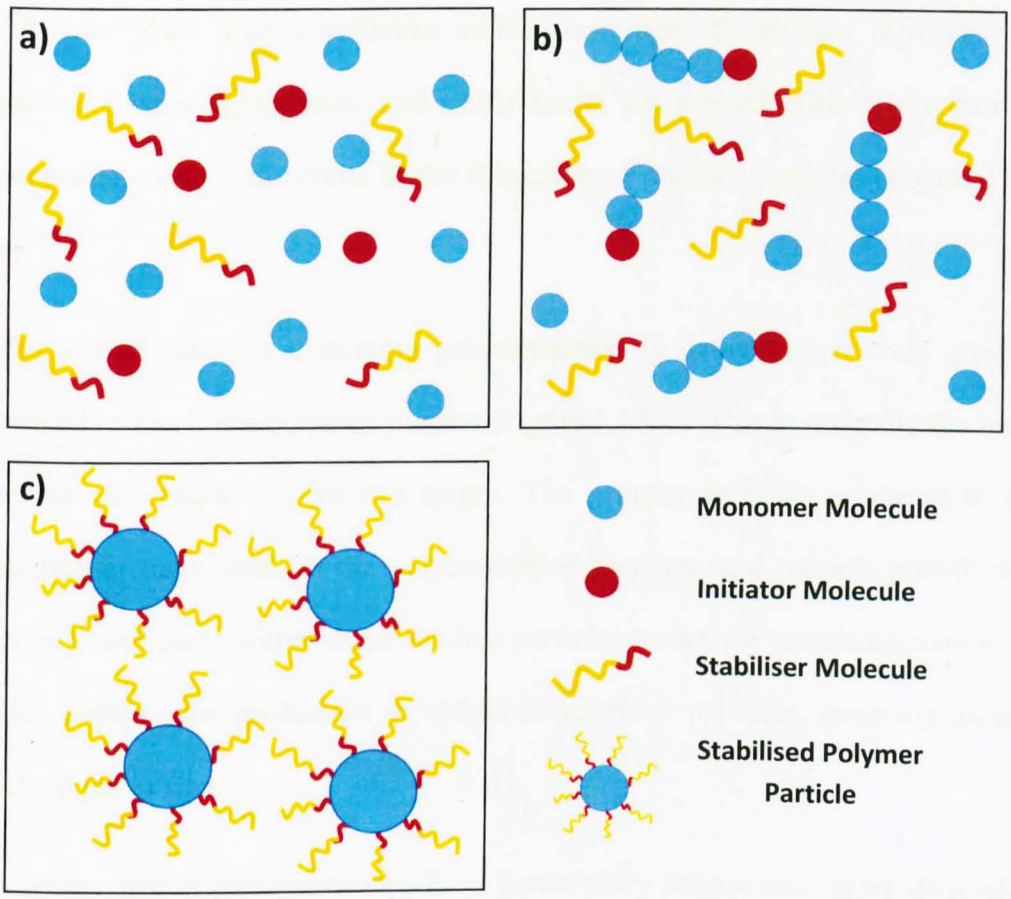


Figure 1.13: Dispersion polymerisation process: a) Monomer, initiator and stabiliser are dissolved in continuous phase of the reaction medium; b) Radicals initiate polymerisation and at critical chain length (J_{crit}) the primary particles precipitate out; c) Polymerisation proceeds with monomer-swollen primary particles, with stabiliser adsorbing at surface *via* the anchor group, providing steric stabilisation and solubility in the reaction medium.[103]

Aggregation of the polymer chains will occur as they precipitate from solution, leading to phase separation at an early stage and the formation of unstable nuclei.[106] The resulting unstable nuclei will rapidly aggregate together, and stabiliser molecules will adsorb to the growing polymer particles. This process will take place until a sufficient surface coverage of stabiliser is reached to prevent further aggregation, and stable nuclei are formed. This is the particle nucleation stage, and results in the formation of primary particles (Figure 1.13, b).[107]

The second stage of dispersion polymerisation is defined as particle growth, which is a much less complex process (Figure 1.13, c). This is generally the more robust and lengthy of the two stages. The primary particles produced in the nucleation stage swell in the polymerisation medium, and particle growth will largely take place within these swollen particles, using the remaining monomer. This leads to the production of stabilised spherical particles, generally around 0.1-10 μm in size.

A wide range of monomers have been successfully polymerised using dispersion polymerisation, and the method has been adopted as an alternative to solution polymerisation of vinyl monomers for use in coating applications.[107]

Dispersion polymerisation will be the focus of a significant body of research within this thesis, and dispersion polymerisation in supercritical carbon dioxide ($scCO_2$) will be discussed in further detail in section 1.3.3 of this chapter.

1.3 Supercritical Fluids

1.3.1 Introduction

A supercritical fluid (SCF) may be defined as the phase of a substance above its critical temperature (T_c) and critical pressure (P_c).[108, 109] A phase diagram can be used to illustrate the various states of a substance and the conditions under which each phase exists. A phase diagram for a pure substance can be used to explain the phenomenon of supercritical fluids (Figure 1.14).[110] The state of the substance is most often described as a function of temperature and pressure, although the critical density can also be taken into account.[111] Lines on a phase diagram indicate the boundaries, at which point phase transitions occur.

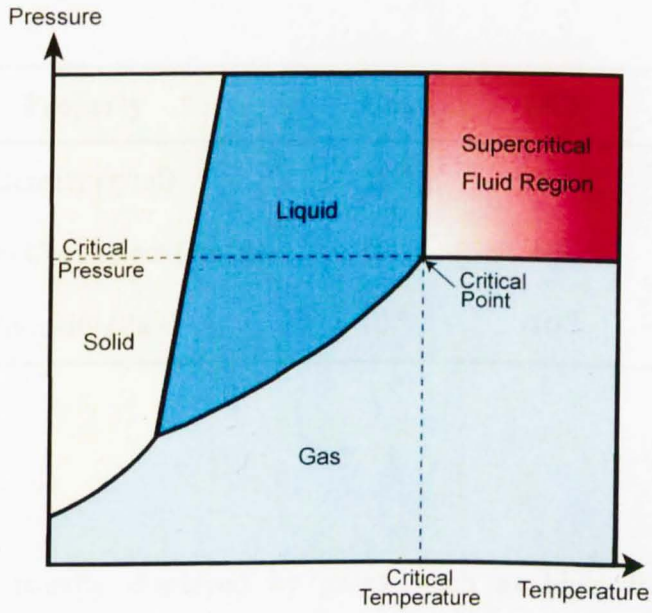


Figure 1.14: Typical phase behaviour diagram for a pure substance, including the supercritical fluid region.

At the triple point, the temperature and pressure are such that the solid, liquid and vapour phases coexist and are in equilibrium with one another. At the critical point, the critical temperature and pressure are reached, and the phase boundary between liquid and vapour is no longer present. At this point, the substance becomes a single phase, defined as the supercritical phase, where the two existing phases become indistinguishable.[112]

Supercritical fluids have lower viscosities than conventional solvents, and they exhibit both gas-like and liquid-like properties, with overall property values lying between that of those expected for classical gases and liquids (Table 1.1).[108]

Table 1.1: A comparison of the typical physical properties of gases, liquids and supercritical fluids.[108]

Property	Gas	SCF	Liquid
Density (g/ml)	10^{-3}	0.3	1
Diffusion Coefficient (cm^2/s)	0.1	10^{-3}	5×10^{-6}
Viscosity (Pa s)	10^{-5}	10^{-4}	10^{-3}

The properties usually displayed by gases, such as high diffusivity, good miscibility with other gases and weak molecular association, are combined with the liquid-like density and ability to dissolve and transport organic compounds.[111]

Increasing the pressure (or decreasing the temperature) of a compound once it is in the supercritical state will result in a corresponding increase in the density of the supercritical fluid.[113] The density is particularly sensitive to small pressure changes near the critical point. Because of the dependence of density on both pressure and temperature, these parameters can be readily and precisely adjusted to tune properties such as the solvent strength of the SCF.

A range of substances with varying critical parameters have been investigated as supercritical fluids (Table 1.2). Substances which possess strong intermolecular forces (*e.g.* water) will have a higher T_c, as will substances with a higher molar mass.[114] The critical pressure and temperature will limit the applications of a particular SCF. Higher values of T_c and P_c will be much more energy intensive and expensive.[108, 115]

Table 1.2: Critical parameters for common substances in the supercritical state.[116]

Compound	Critical Temperature (T_c)/ °C	Critical Pressure (P_c)/ bar (psi)	Critical Density/ g cm^{-3}
Carbon dioxide	31.1	74 (1073)	0.47
Ethane	32.8	49 (711)	0.22
Propane	97.2	43 (624)	0.22
Ammonia	132.5	113 (1639)	0.24
Water	374.2	221 (3205)	0.32

1.3.2 Supercritical Carbon Dioxide ($scCO_2$)

Supercritical carbon dioxide ($scCO_2$) is one of the most promising SCFs, and is continually attracting attention as a potentially viable 'green' solvent. It is relatively non-toxic, non-flammable and relatively inert towards reactive compounds. The environmentally benign properties of $scCO_2$ make it a potential green alternative to traditional organic solvents currently used in polymer synthesis.[117] Additionally, CO_2 has an easily attainable critical point (31.1 °C, 73.8 bar) when compared to SCFs such as water (Table 1.2). Carbon dioxide is an inexpensive material, and can be recycled from other industrial processes where it is obtained as a by-product. In this manner, net emissions of CO_2 into the atmosphere are not increased.

As previously discussed, $scCO_2$ also possesses a high diffusivity, low viscosity and tuneable solvating power, rendering it an effective alternative to conventional organic solvents. It has been extensively investigated by both industry and academia, and used in a number of reactions including hydroformylations,[118] Friedel-Crafts alkylations,[119] and as an extraction medium for caffeine.[120]

Recently, $scCO_2$ has also found application as a medium for polymer synthesis and processing.[121-124] This is a result of a number of properties, in addition to the environmental benefits. Polymer is easily recovered from the reaction medium, as $scCO_2$ allows for simple product separation upon depressurisation, producing a material free of solvent residues. This is a desirable property for various applications, reducing the need for energy-intensive drying procedures.[125, 126] The

tuneable density of $scCO_2$ can also be exploited to tune the solvating power of the reaction medium and separate specific polymer fractions individually.[127]

Also, the high diffusivity of $scCO_2$ makes it possible for CO_2 molecules to penetrate through polymer chains. This can cause depression of the glass transition temperature (T_g) as the CO_2 lowers the thermal energy required for chain movement. This effect is known as plasticisation.[128-131] Plasticisation has enabled techniques such as polymer foaming, blending and impregnation to be performed in $scCO_2$, and could potentially also enhance the diffusion of monomer and initiator into the polymer phase in heterogeneous polymerisations.[116, 132-134]

1.3.3 Dispersion Polymerisations in $scCO_2$

Dispersion polymerisations are highly suited to adaptation in $scCO_2$ because of the miscibility of the vast majority of monomers in the continuous phase at modest pressures, and the low solubility of most high molecular weight materials.[117] With the aid of a stabiliser, dispersion polymerisation enables the production of free-flowing powder polymers with a high yield and uniform, spherical particles. Employing a suitable stabiliser for dispersion polymerisation in $scCO_2$ is crucial. This is achieved through the application of ionic or steric stabilisers. Ionic stabilisers are not effective in low/non-polar solvents such as $scCO_2$, and so steric stabilisation must be employed, using polymeric surfactants. As described in section 1.2.6, polymeric stabilisers are required in dispersion

polymerisations to produce a stable latex of growing polymer particles and allow solubilisation of these particles in the continuous phase.

The function of a stabiliser is to provide a method of solvation for the macromolecules within the solvent system. Stabilisers often tend to be amphiphilic, composed of two components. The first is a polymer-philic anchoring group which will attach to the surface of the growing polymer particle *via* physical adsorption or chemical grafting, whilst the second component is tailored to possess an affinity for the continuous phase (CO_2-philic) and allows solubilisation of the polymers within the reaction medium as it partitions at the polymer/solvent interface.[103]

Stabilisers enable the dispersion of the polymer particles throughout the system by surrounding the surface of the individual polymer particles and allowing solubilisation in the continuous phase. In addition, the surfactants employ a steric stabilisation mechanism to prevent aggregation of the growing polymer particles. Steric stabilisation is a result of the increased stabiliser segment density experienced when two polymer particles approach and the polymer sheaths interpenetrate or are compressed (Figure 1.15).[135] This region of increased stabiliser concentration generates an osmotic pressure, and diffusion of solvent into this region produces a repulsive force, pushing the polymer particles apart. The concentration of the solvated stabiliser layer needs to be strong enough to generate an osmotic pressure able to overcome attractive Van der Waals forces between particles, allowing repulsion to dominate and resulting in a stable system which remains in a dispersed state.

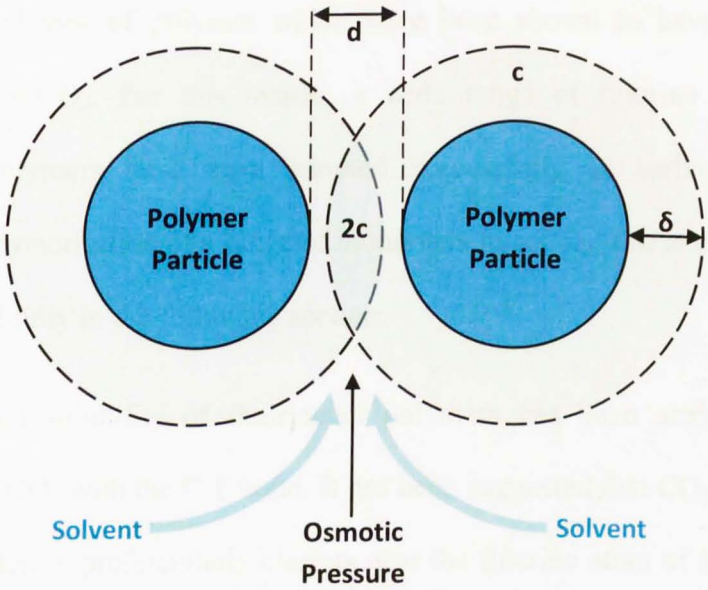


Figure 1.15: The close approach of two polymer particles, and the resulting process of steric stabilisation. The stabiliser chains of the polymer particles interpenetrate, increasing the concentration of the stabiliser chains within the layer. Osmotic pressure is generated, and affects the migration of solvent molecules into this region, forcing the polymer particles apart, and preventing agglomeration.[105] δ = thickness of stabiliser layer in solution; c = concentration of stabiliser; d = distance between particles.

Selection of an effective stabiliser is critical to the production of a successful dispersion polymerisation in $scCO_2$. The stabiliser must possess a CO_2-soluble component, and this is an issue when employing polymeric surfactants, which are notoriously insoluble in CO_2. The limited solubility of most polymers is believed to be related to their polarity, and the fact that CO_2 possesses a quadrupole, despite having no permanent dipole.[136] Fluorinated and silicone-based polymers

are the two classes of polymer which have been shown to have appreciable solubility in $scCO_2$. For this reason, a wide range of fluorine and silicone containing polymers have been adopted successfully as surfactants in the dispersion polymerisation of a range of monomers in $scCO_2$. These stabilisers will be considered fully in the following section.

The significant solubility of fluorinated polymers has been attributed to the interaction of CO_2 with the C-F bond. It has been suggested that CO_2 either forms a weak complex or preferentially clusters near the fluorine atom of the C-F bond, which is more polar than corresponding C-H bonds, so that the fluorinated side chains effectively shield the hydrocarbon main chain from interaction.[116, 137-139] Silicone polymers, although generally not as soluble as fluorinated polymers, are proposed to exhibit good CO_2-solubility as a result of the low cohesive energy density, which reduces the free energy of mixing.[140]

Stabilisers with homopolymer, block copolymer, graft copolymer and random copolymer architectures have all been investigated for use in polymerisations in $scCO_2$. In the following section, the structure and stabilising ability of a range of these materials will be considered.

1.3.3.1 Homopolymer Stabilisers

DeSimone and coworkers were the first to develop a successful dispersion polymerisation method for methyl methacrylate (MMA) using a fluorinated stabiliser, Poly(1, 1-dihydroperfluorooctyl acrylate), PFOA.[17] The polymer consists of an acrylic backbone and a fluorinated side chain (Figure 1.16, a).

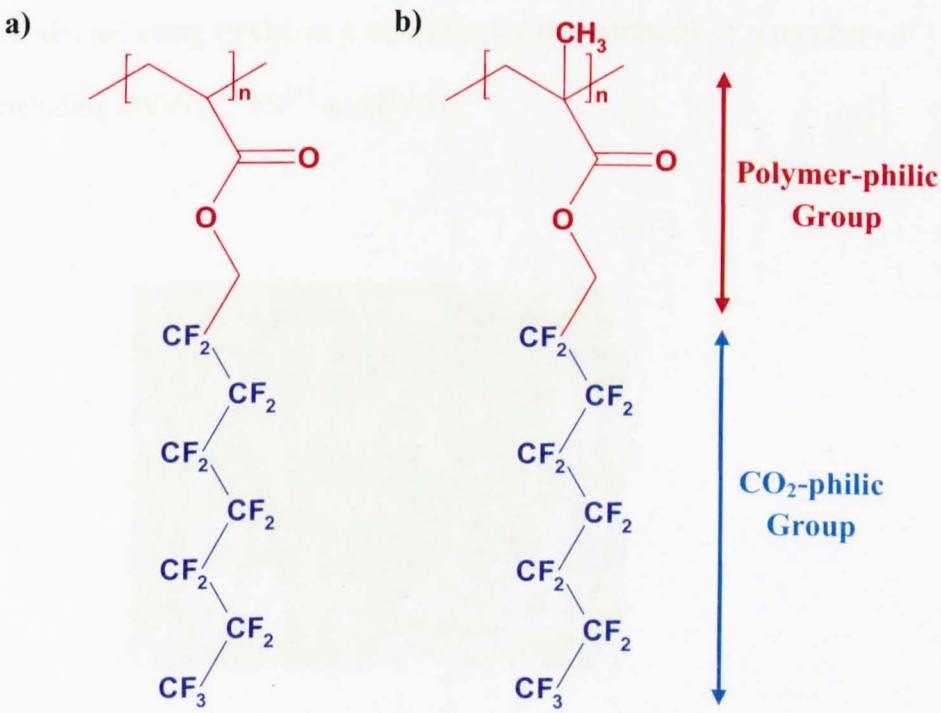


Figure 1.16: Structure of a) homopolymer stabiliser PFOA, with polymer-philic backbone and fluorinated CO_2-philic side chains[17] and b) methacrylate analogue, PFOMA.[141]

The hydrocarbon backbone of PFOA acts as the polymer-philic portion, whilst the CO_2-philic fluorinated groups project into the continuous phase and enable steric stabilisation, preventing flocculation. The stabiliser was employed in the dispersion polymerisation of MMA, producing a free-flowing powder with high molecular weight and conversion.[142] Scanning electron microscopy (SEM) revealed a uniform, spherical morphology with particle size diameter of 1.2-2.5 μm (Figure 1.17). Following this work, successful dispersion polymerisations have been conducted using PFOA as a stabiliser for the synthesis of a number of polymers, including PNVP,[143] PS[141] and PVAc.[144]

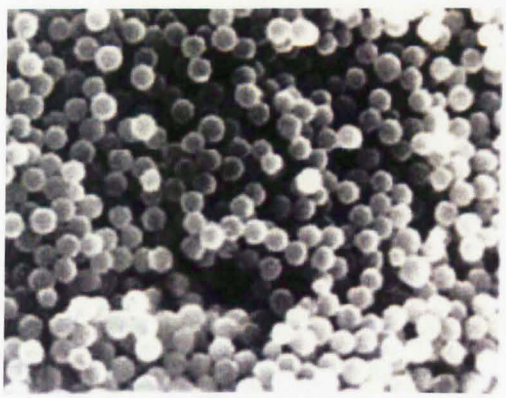


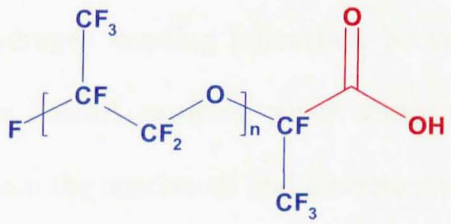
Figure 1.17: Spherical particle morphology of PMMA products obtained using PFOA in dispersion polymerisation (1.2 wt % PFOA).[142]

Poly(1,1-dihydroperfluorooctyl methacrylate), also known as PFOMA, is a methacrylate analogue of PFOA that has been developed (Figure 1.16, b). This

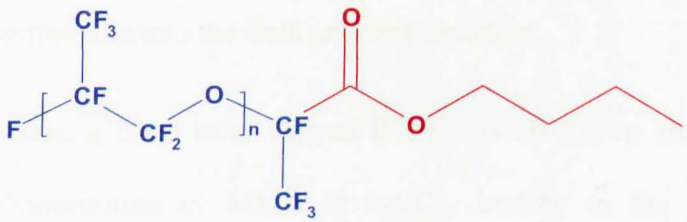
homopolymer stabiliser has also been used with success in the dispersion polymerisation of PS, producing micron sized particles.[141]

Functionalised homopolymers are a second class of homopolymer stabilisers that have met with success in dispersion polymerisations in $scCO_2$ (Figure 1.18).

a)



b)



c)

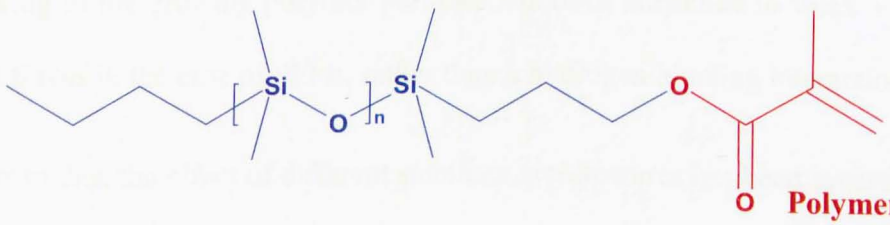


Figure 1.18: Functionalised homopolymer stabilisers: a) Krytox-157 FSL;[145] b) Butyl ester capped PFPE;[146] c) PDMS-mMA.[147]

Krytox-157 FSL is a commercially available acid terminated perfluoropolyether (PFPE), in which the polymer-philic head group consists of a carboxylic acid which is capable of hydrogen bonding (Figure 1.18, a).

The successful polymerisation of MMA in $scCO_2$ using Krytox-157 FSL was reported by Christian *et al.* and a high molecular weight PMMA product with high yield and spherical microparticle formation was observed.[145] FT-IR was also used to confirm a hydrogen bonding interaction between the carboxylic acid terminal group and the PMMA particles, which causes effective partitioning of the PFPE chains between the continuous and discrete phase. A key advantage of Krytox-157 FSL is the ability of the polymer to act as a stabiliser without being chemically incorporated into the final polymer structure.

In addition to this, a butyl ester capped PFPE has also been employed in the dispersion polymerisation of MMA in $scCO_2$, leading to the production of spherical microparticles (Figure 1.18, b).[146] The mechanism of stabiliser anchoring to the growing polymer particles has been attributed to weak Van der Waals forces in the case of PFPE, rather than a hydrogen bonding interaction.

Further to this, the effect of different stabiliser architectures has been investigated, incorporating three different types of PMMA-philic terminal head groups and employing PFPE chains as the CO_2-philic component.[148] An alcohol, acetate and methacrylate head group were all considered, and compared to the polymer product obtained in the absence of stabiliser. It was observed that in comparison to a PFPE-alcohol stabiliser, incorporation of a small anchor group such as an

acetate group, or a reactive methacrylate unit, had a significant impact on the dispersion polymerisation of MMA in $scCO_2$, leading to improvements in yield, molecular weight and morphology of the final product. PFPE-alcohol is likely to self-associate as a result of the hydroxyl group, preventing it from sufficiently anchoring to PMMA. Incorporation of an acetate group enables interaction with the growing PMMA particles through a weak Van der Waals interaction. Further to this, application of a methacrylate-capped PFPE dramatically enhanced the anchoring ability, as the stabiliser is able to covalently graft to the growing PMMA chains through this reactive end-group. This study highlights the importance of choosing an effective stabiliser anchor group in order to effectively support dispersion polymerisation in $scCO_2$.

Silicone polymers are also attractive as stabilisers, possessing favourable CO_2-solubility but being much less expensive than fluorinated materials. In 1996, Shaffer *et al.* reported the dispersion polymerisation of MMA in CO_2 using a commercially available methacrylate-terminated poly(dimethylsiloxane) macromonomer, PDMS-mMA (Figure 1.18, c).[147] The stabiliser possesses a reactive terminal group, which allows chemical incorporation into the growing polymer particle. High molecular weight PMMA product with a good yield and uniform, spherical particles were obtained, but increased stabiliser loadings were typically required for good control over particle morphology (3.5-16 wt %). It was also observed that only a fraction of the PDMS-mMA was grafted to the PMMA particles (< 0.7 wt % PDMS-mMA).

Polymerisation in the presence of a PDMS homopolymer, which lacks the reactive methacrylate end-group, was not very effective in the dispersion polymerisation of MMA, highlighting the importance of the terminal group in stabilising ability.[147] In addition, polymerisation of VAc in $scCO_2$ has been found to be unsuccessful, proving the weak anchoring ability of PDMS-mMA to be insufficient for stabilising the synthesis of PVAc particles.[144]

1.3.3.2 Block Copolymer Stabilisers

Block copolymers have been found to act as successful stabilisers, being composed of a CO_2-philic block and a polymer-philic/anchoring block. As a result, a number of block copolymer structures have been extensively employed as stabilisers for dispersion polymerisation in $scCO_2$ (Figure 1.19).

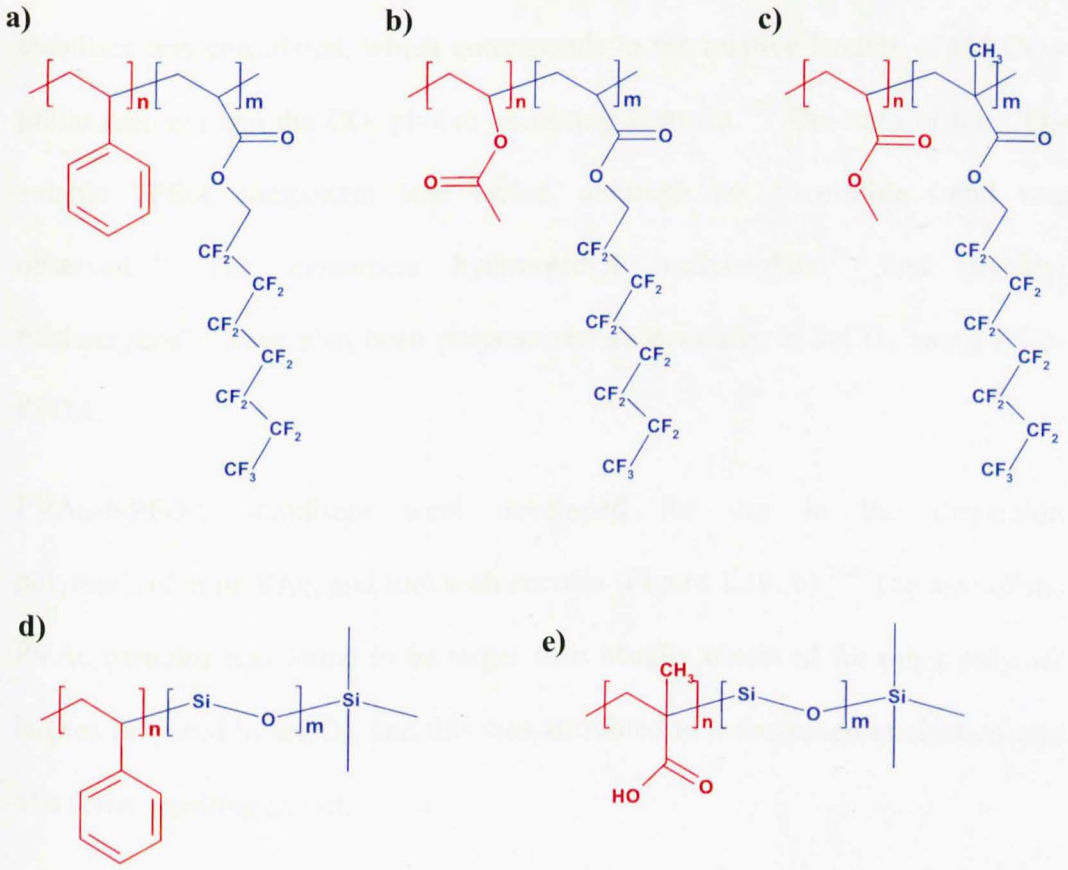


Figure 1.19: Key block copolymer stabiliser structures: a) PS-*b*-PFOA;[149] b) PVAc-*b*-PFOA;[144] c) PMMA-*b*-PFOMA;[150, 151] d) PS-*b*-PDMS;[152] e) PMA-*b*-PDMS.[153]

Canelas *et al.* first showed that a stabiliser of PS-*b*-PFOA was effective for the dispersion polymerisation of styrene in $scCO_2$ (Figure 1.19, a).[149] The stabiliser was used to produce spherical microparticles with high molecular weight, and the polymer product was observed to depend upon the molecular weight of the stabiliser employed. Increasing the length of both blocks led to a corresponding decrease in particle size distribution and diameter, with diameters ranging from 0.24-0.4 μm. In addition, the effect of the anchor-to-soluble balance (ASB) of the stabiliser was considered, which corresponds to the relative lengths of the CO_2-philic segment and the CO_2-phobic anchoring segment.[124] The ratio of the CO_2-soluble PFOA component was varied, although no discernible trend was observed.[149] The monomers hydroxyethyl methacrylate[154] and glycidyl methacrylate[155] have also been polymerised successfully in $scCO_2$ using PS-*b*-PFOA.

PVAc-*b*-PFOA stabilisers were developed for use in the dispersion polymerisation of VAc, and met with success (Figure 1.19, b).[144] The size of the PVAc particles was found to be larger than usually observed for other polymer latexes prepared in $scCO_2$, and this was attributed to a decreased nucleation rate and fewer resulting nuclei.

Dispersion polymerisations of the monomers MMA[150] and divinylbenzene[151] have been investigated using stabilisers of PMMA-*b*-PFOMA. The molecular weight of the polymeric stabiliser and the anchor-to-soluble balance were found to have a significant effect on the resulting yield and particle morphology in both cases. The length and CO_2-philicity of the stabiliser was successfully controlled through

variation of the fluorinated block. Higher molecular weight block copolymers and more highly fluorinated block copolymers were observed to be much more effective stabilisers.

Canelas and DeSimone also studied the application of PS-*b*-PDMS block copolymers, using the PDMS block as the CO_2-philic group (Figure 1.19, d).[152] The authors observed an increase in particle size as the stabiliser loading was decreased, with particle size diameters ranging from 0.31-1.15 μm. CO_2 density was also observed to have a significant impact on particle morphology, whilst the presence of heptane had a negative impact on the particle morphology. The ASB was also found to be crucial in producing a stable dispersion polymerisation.

Yates *et al.* reported the synthesis of poly(methacrylic acid)-*b*-PDMS block copolymers, consisting of a CO_2-philic PDMS block and a hydrophilic PMA block (Figure 1.19, e).[153] Uniform PMMA particles were successfully obtained. The unique property of this stabiliser is that it can be employed to form water-dispersible PMMA powders. This is a result of the nature of the surfactant, which can provide stabilisation in both CO_2 and water.

1.3.3.3 Graft Copolymer Stabilisers

Graft/comb-type stabiliser architectures have also found success in dispersion polymerisations in $scCO_2$, consisting of a polymer-philic backbone and CO_2-philic grafted polymer chains (Figure 1.20).

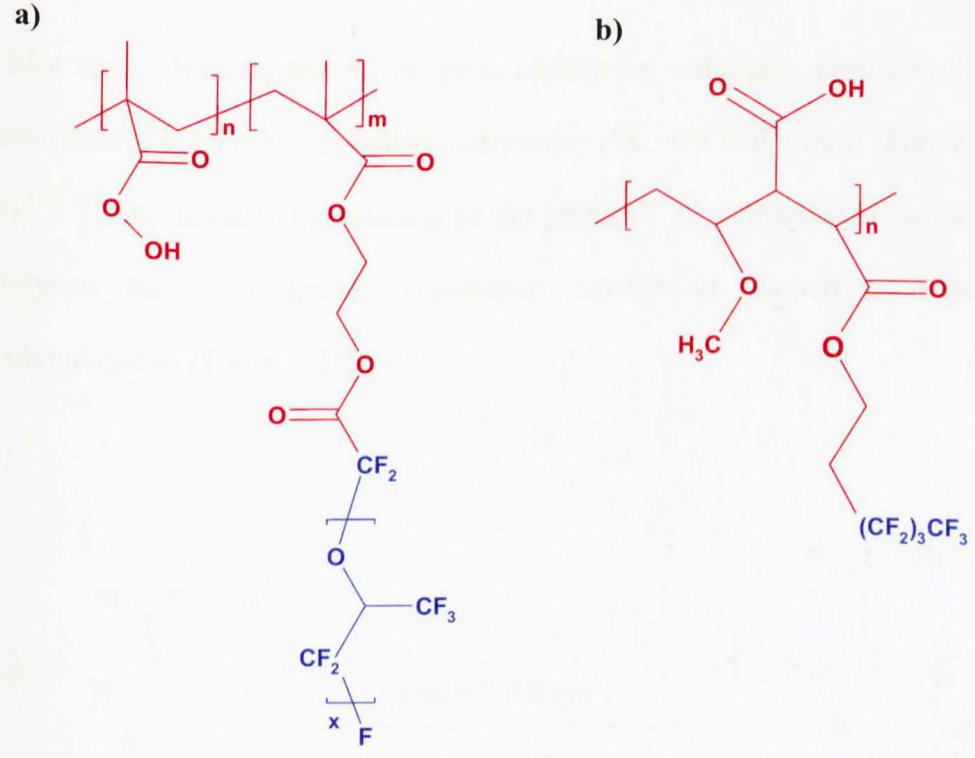


Figure 1.20: Graft copolymer stabilisers: a) (PMMA-*co*-HEMA)-*g*-PFPO;[156] b) Poly(methyl vinyl ether-*alt*-maleic anhydride) derived graft structure.[157, 158]

Lepilleur and Beckman investigated a series of stabilisers based on a CO_2-phobic poly(MMA-*b*-hydroxyethylmethacrylate) backbone, with varying percentages of a CO_2-philic poly(perfluoropropylene oxide) graft (Figure 1.20, a).[156] The stabiliser was found to be active in the dispersion polymerisation of MMA, leading to the production of micron-sized particles in good yields and with high molecular weight.

Giles *et al.* investigated novel graft copolymer stabilisers synthesised from poly(methyl vinyl ether-*alt*-maleic anhydride) (M_n =79 800 g/mol) (Figure 1.20, b).[157, 158] On thermal ring opening in the presence of a fluorinated alcohol, the polymer formed a grafted copolymer capable of supporting dispersion polymerisation (Figure 1.21).

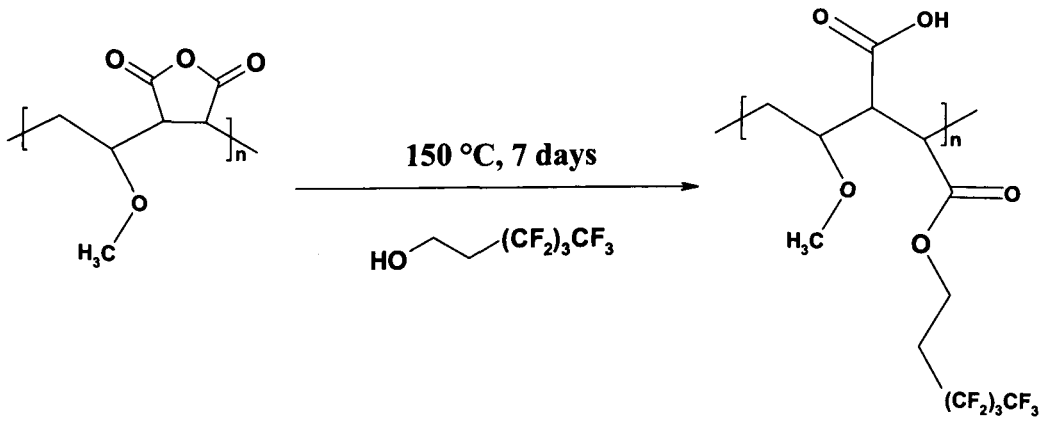


Figure 1.21: Thermal ring opening of poly(methyl vinyl ether-*alt*-maleic anhydride).[158]

The surfactants were found to be effective in the stabilisation of dispersion polymerisations of MMA in $scCO_2$, stabilising through a hydrogen bonding interaction between the carbonyl group of methyl methacrylate and carboxylic acid groups on the stabiliser. Stabiliser activity was found to be independent of backbone chain length, whilst in contrast, the addition of pendant hydrocarbon moieties to the grafted chains had a significant impact.[157]

1.3.3.4 Random Copolymer Stabilisers

Random copolymers have also been reported as effective stabilisers, and a number of random copolymers have been employed successfully for dispersion polymerisations in $scCO_2$ (Figure 1.22).

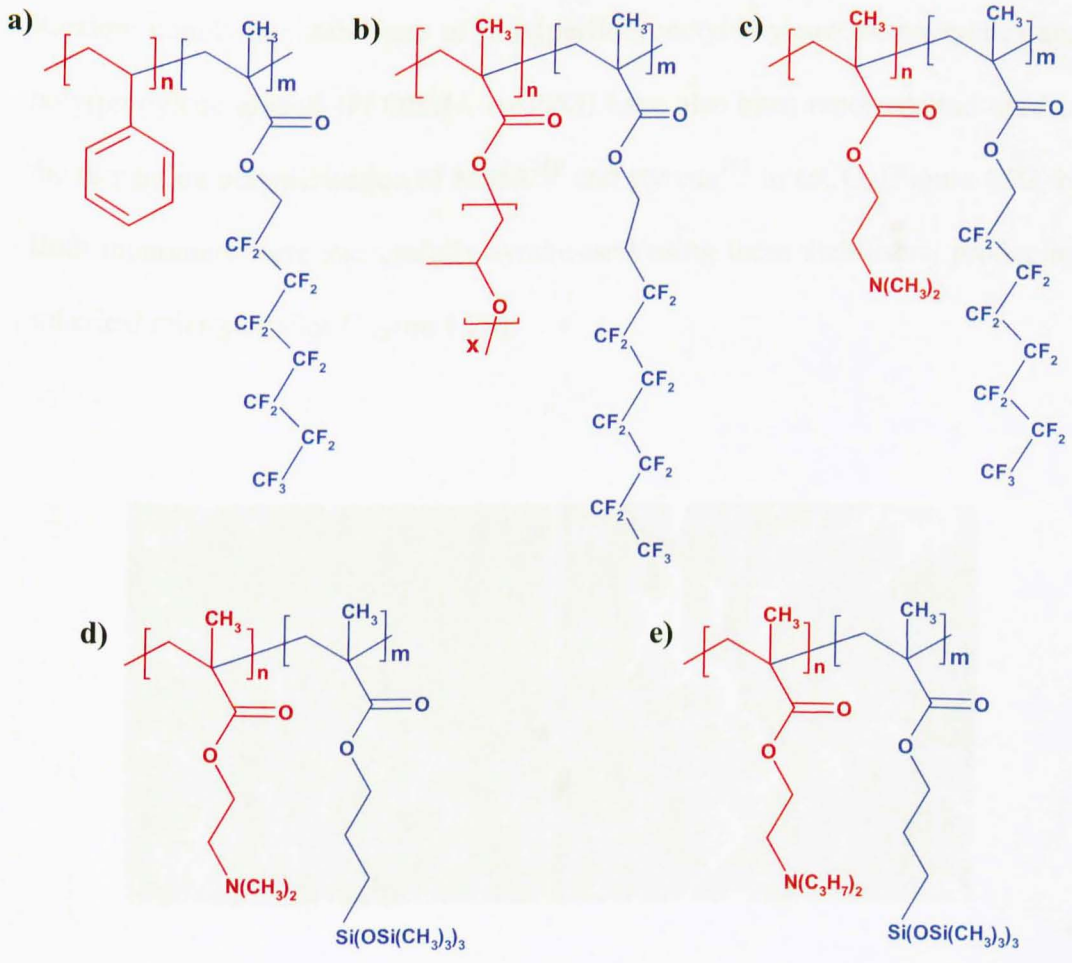


Figure 1.22: Random copolymer stabilisers: a) PS-*co*-PFOMA;[159] b) PPG-*co*-PFOEMA;[160, 161] c) PDMAEMA-*co*-PFOMA;[162] d) PDMAEMA-*co*-PSiMA;[163] e) PDPAEMA-*co*-PSiMA.[163]

Shiho *et al.* synthesised random copolymers of PS and PFOMA, which were subsequently applied in the dispersion polymerisation of styrene (Figure 1.22, a).[159] It was found that the fluorinated random copolymers were highly effective stabilisers, generating micron-sized polystyrene particles at high yields. Particle size was observed to decrease with a corresponding increase in the proportion of fluorinated acrylate within the stabiliser.

Random copolymer stabilisers of poly(perfluorooctylethylene methacrylate) and poly(propylene glycol) (PFOEMA-*co*-PPG) have also been reported, and used in the dispersion polymerisation of MMA[160] and styrene[161] in $scCO_2$ (Figure 1.22, b). Both monomers were successfully synthesised using these stabilisers, producing spherical microparticles (Figure 1.23).

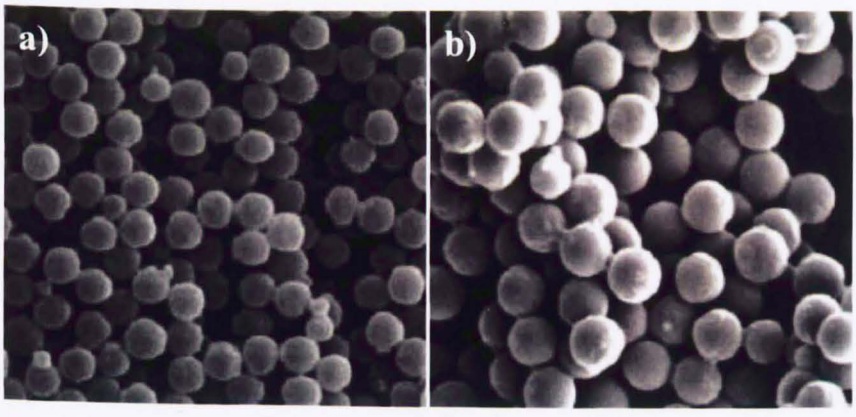


Figure 1.23: PMMA particles synthesised with random copolymers stabilisers at 5 wt % loading and varying composition: a) 52 % FOEMA and b) 75 % FOEMA.

More recently, Yuvaraj *et al.* demonstrated the synthesis of random copolymer stabilisers of PFOMA-*co*-PDMAEMA and their application in the synthesis of PS particles (Figure 1.22, c).[162] The DMAEMA units acted as the polymer-philic anchor group, allowing adsorption to the PS particles, and subsequent stabilisation.

The same group also reported the synthesis of non-fluorous random copolymers through the copolymerisation of 3-[tris(trimethylsilyloxy)silyl]propyl methacrylate with DMAEMA and diisopropylaminoethyl methacrylate (DPAEMA), forming poly(SiMA-*co*-DMAEMA) and poly(SiMA-*co*-DPAEMA) (Figure 1.22, d-e).[163] The stabilisers were prepared with different co-monomer compositions and employed in the dispersion polymerisation of styrene in $scCO_2$. Both composition and stabiliser concentration were found to affect the final polymer product. In addition, poly(SiMA-*co*-DPAEMA) provided better stabilisation in comparison to poly(SiMA-*co*-DMAEMA), which the authors proposed was a result of increased methyl branching in the DPAEMA pendant group.

1.3.3.5 Hydrocarbon Stabilisers

The majority of surfactants discussed so far have been predominantly composed of fluorinated and silicone units, which provide enhanced CO_2-solubility. However, these materials are expensive, and also potentially toxic, making them largely unsuitable for wide-scale industrial use. Economically viable alternatives are required if polymerisations in $scCO_2$ are to become a possibility.

Recently, considerable academic research has focused on the development of inexpensive hydrocarbon stabilisers. A number of polymers have already been identified as possessing promising CO_2-philicity, with the potential to act as effective stabilisers.[164-170] The phase behaviour and stabilising ability of hydrocarbon materials synthesised by a number of research groups will be considered in Chapter 3. The focus of this thesis is the study of potential new hydrocarbon stabilisers for application in $scCO_2$ and will form the main body of this work.

1.4 Research Aims

One of the continuing challenges in the application of $scCO_2$ as a solvent for polymerisation is the design of CO_2-soluble stabilisers which are inexpensive, non-toxic and efficient. The focus of this thesis is to address this issue and investigate the design of a range of novel hydrocarbon stabilisers for dispersion polymerisations in $scCO_2$.

Chapter 3 presents the synthesis of hydrocarbon stabilisers of poly(vinyl acetate) (PVAc) and poly(vinyl pivalate) (PVPi) using the controlled technique of RAFT polymerisation. A series of stabiliser materials with defined molecular weight and low polydispersity are presented, with various molecular weights and monomer compositions. The phase behaviour of these stabilisers is investigated using a high pressure variable volume view cell, and the solubility of these materials in $scCO_2$ is discussed.

Chapter 4 aims to determine the efficacy of these previously synthesised materials as stabilisers in dispersion polymerisations in $scCO_2$. A variety of stabilisers are tested, and the effect of stabiliser molecular weight and composition on the dispersion product is compared, along with additional parameters such as stabiliser loading.

Finally, Chapter 5 examines a number of additional areas of research dealing with the architecture of the stabiliser. A series of block copolymers are compared and contrasted for solubility and stabilising ability in $scCO_2$. In addition, the impact of changes to the stabiliser end groups are considered.

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Chapter 2: Experimental and Characterisation Techniques

This chapter describes the experimental and characterisation techniques employed throughout the thesis. There are two main sections to this chapter. The first half of the chapter is concerned with experimental techniques employed, and in particular the high pressure equipment used to carry out dispersion polymerisations in $scCO_2$. For the majority of high pressure reactions, stainless steel clamp-sealed vessels were used and this section focuses on these high pressure vessels.

The second half of the chapter details the characterisation techniques used to analyse the materials synthesised in this thesis. Stabilisers were fully characterised to determine their composition and molecular weights. The dispersion products obtained from polymerisation using $scCO_2$ were also analysed to determine conversion, molecular weight and particle morphology.

2.1 High Pressure Equipment

2.1.1 General High Pressure Setup

A typical high pressure system will consist of a means of supplying pressure to the system (CO_2 pump), a high pressure vessel for conducting reactions, and monitoring equipment necessary to monitor the pressure and temperature. A standard high pressure system designed to conduct polymerisations in $scCO_2$ is outlined in schematic form (Figure 2.1).[1-3]

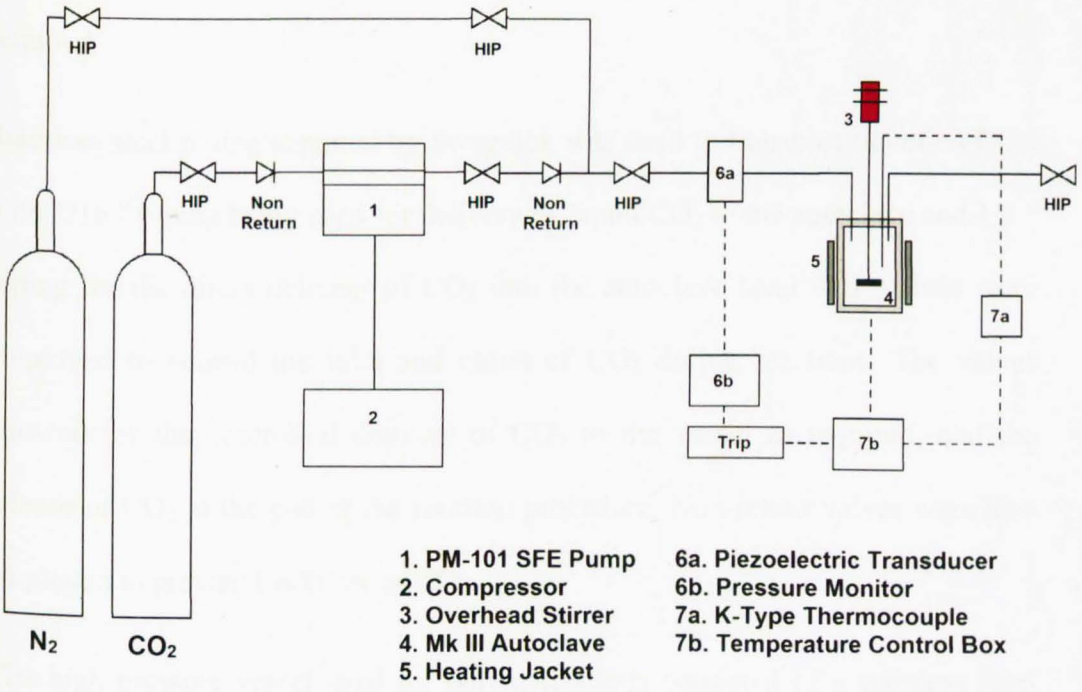


Figure 2.1: Schematic diagram of high pressure rig setup.

The PM-101 SFE Pickel pump, supplied by New Ways of Analytics, was used as the means of delivering compressed CO_2 to the reaction vessels. The pump possesses a gas input valve and a refrigerator unit for gas liquefaction. Output pressure is controlled by compressed air (6 bar), which compresses the liquefied CO_2 by means of a high surface area ratio piston setup (111:1). This is regulated *via* a regulator knob on the front of the pump. The pump draws gas from a supply cylinder, where it is condensed into liquid CO_2. The compressed air drives a large piston connected to a smaller piston, and the difference in surface area of the two pistons allows the relatively low air pressure to compress the liquid CO_2 to the desired pressure, and the pressurised liquid is fed into the reaction vessel as required.

Stainless steel piping supplied by Swagelok was used to transport liquefied CO_2, with 1/16 " piping being used for delivery of liquid CO_2 to the autoclave and 1/8 " piping for the direct delivery of CO_2 into the autoclave head. HIP valves were employed to control the inlet and outlet of CO_2 during reactions. The valves allowed for the controlled delivery of CO_2 to the vessel as required, and the release of CO_2 at the end of the reaction procedure. Non-return valves were also employed to prevent backflow of CO_2.

The high pressure vessel used for polymerisations consisted of a stainless steel autoclave which will be discussed in the following section.

2.1.2 MK III Clamp Sealed Autoclave

All dispersion polymerisation reactions reported in this thesis employed a 60 mL, clamp-sealed Mk III autoclave made of stainless steel. The autoclave was designed in-house at the University of Nottingham and is detailed extensively elsewhere.[4, 5] The autoclave consists of a stainless steel base and a head attachment which make up the main autoclave high pressure reaction chamber. A photograph and schematic diagram of the Mk III autoclave and the safety key/clamp system are shown in Figure 2.2 and 2.3 respectively.

There are two main components to the vessel; the autoclave head and the autoclave base. The head is attached to the base using a stainless steel clamp, safety key, and polymeric O-ring (Figure 2.4).

The polymeric O-ring (EPDM) and clamp are used to seal the head of the autoclave to the body under high pressure. The use of a metal-rubber seal rather than a direct metal-metal seal prevents damage to the stainless steel autoclave through wear and tear to the stainless steel components. The O-ring sits in a grooved seal bed at the top of the autoclave body. The clamp is used to lock the two sections of the autoclave unit together, and utilises a hand-tightened screw mechanism to secure the clamp firmly in place. Use of the EPDM O-rings and stainless steel clamp mechanism for sealing the vessel makes the Mk III autoclave suitable for pressure up to 300 bar at 300 °C.

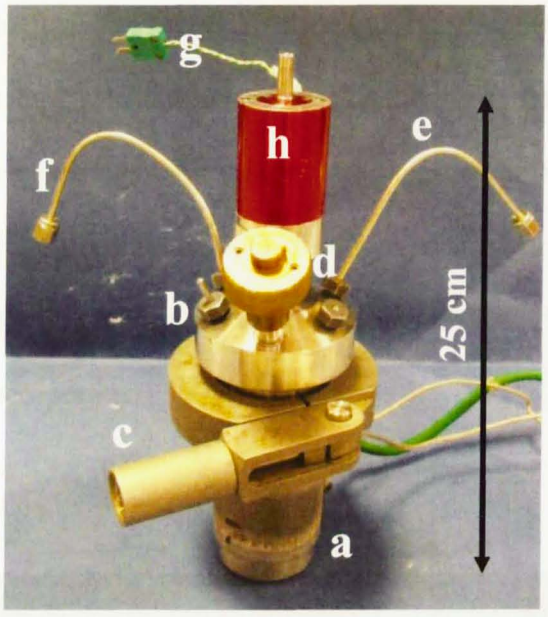


Figure 2.2: Mk III autoclave and components consisting of (a) autoclave base; (b) autoclave head; (c) clamp; (d) safety valve; (e) inlet pipe; (f) outlet pipe; (g) thermocouple; (h) magnetically driven overhead stirrer.

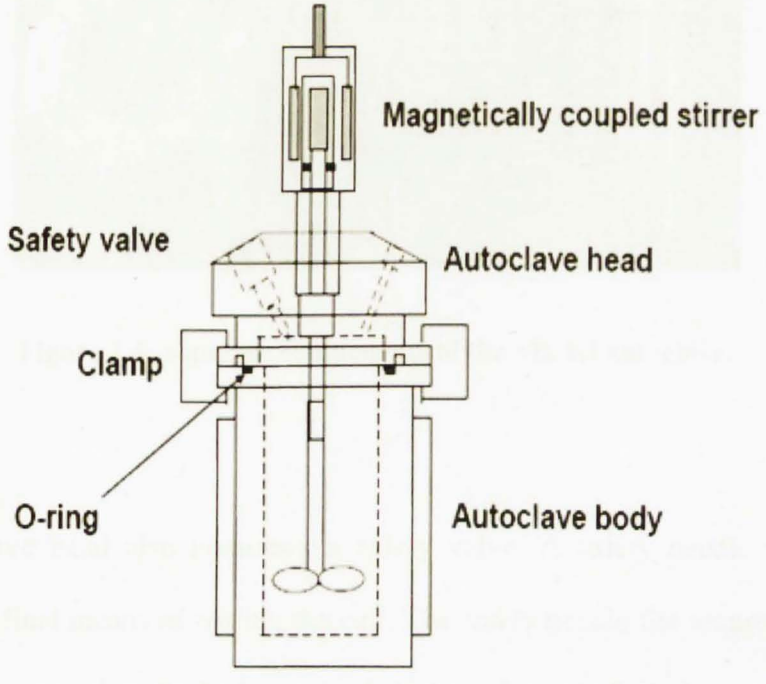


Figure 2.3: Schematic diagram of the Mk III autoclave.

The head of the autoclave consists of five main ports. Three of these are used for the inlet tap, outlet tap and thermocouple. The inlet tap connects to a pressure transducer to allow constant monitoring of the pressure within the system. The outlet tap allows for easy removal of CO_2 from the reaction vessel. The remaining two ports are sealed with metal plugs which can be removed if additional features should need to be incorporated.

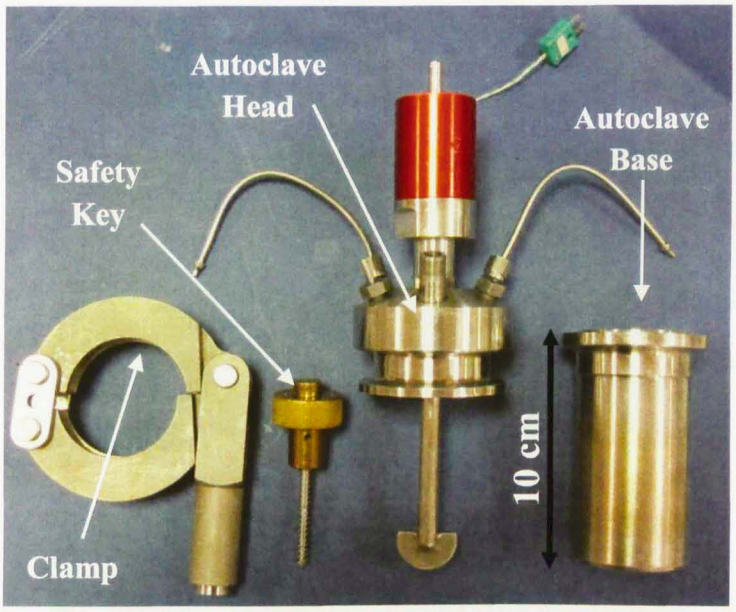


Figure 2.4: Separate components of the Mk III autoclave.

The autoclave head also possesses a safety valve. A safety needle is used to provide the final means of sealing the cell. The safety needle fits securely into the safety valve using the attached pinwheel. If the safety needle is loosened slightly whilst the vessel is under pressure with CO_2, a small hole opens in the autoclave

head *via* the safety valve, which allows the CO_2 to escape gradually. This is a useful means of protection if there is residual gas trapped within the cell. The pinwheel and safety needle combine to form the safety key, which is unique to each autoclave and is the means by which the clamp is tightened into position during assembly (Figure 2.5). One of the design features of this component is that the safety key/valve must be loosened and removed before the clamp can be opened and the autoclave taken apart. This ensures all residual pressure is released before the vessel is fully opened.

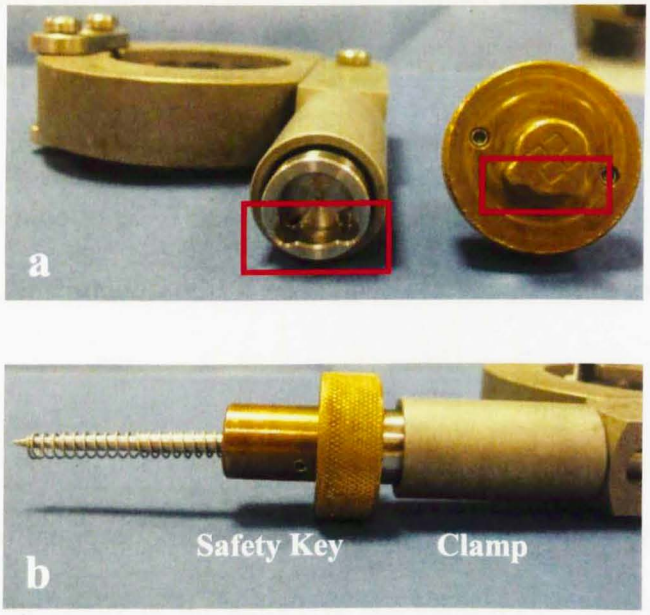


Figure 2.5: Unique safety key and clamp feature of Mk III autoclave. (a) Clamp and safety pinwheel with unique key design which specifically fits the partner clamp; (b) Example of pinwheel and safety needle being employed as the key for the clamp.

Piezoelectric transducers were used to monitor the reaction pressure. A piezoelectric transducer uses the piezoelectric effect to monitor the pressure input signal by converting it to an electrical output signal. The transducer is equipped with a quartz crystal which acts as the piezoelectric element. This crystal experiences proportional strain under pressure, which generates electrical output representative of the pressure of the system. A digital readout unit enables the output of the transducer, and subsequently the pressure of the system, to be effectively monitored.

A custom-made heating jacket (Watlow) which fits around the exterior of the Mk III autoclave body provides excellent thermal contact for efficient heating during reactions. A K-type thermocouple extends into the autoclave cavity *via* one of the five main ports in the autoclave head and allows the internal temperature of the autoclave to be monitored. The thermocouple is connected to a digital heating controller (CAL Instruments 3300) and allows the temperature to be adjusted as required.

A magnetically coupled overhead stirrer is built into the head of the autoclave and allows stirring of the reaction contents within the vessel to take place. The stirrer is screwed into the centre of the autoclave head and sealed with a small O-ring. The shaft of the stirrer extends downwards into the main body of the vessel, where a stirrer blade is attached. An overhead stirring motor (IKA Eurostar Digital) is magnetically connected to the autoclave stirrer shaft during the experimental procedure and enables rotation of the stirrer blade between 50-2000 rpm to ensure efficient mixing during the polymerisation process. A trip switch is

incorporated into the final setup to ensure that if the pressure within the vessel reaches above a 345 bar limit, the power to the temperature controller and heating jacket will be automatically disabled.

2.1.3 Procedure for Dispersion Polymerisation in $scCO_2$

A standard polymerisation procedure was used for the dispersion polymerisation of 1-vinyl-2-pyrollidone (NVP) and other monomers in $scCO_2$. A schematic outline of this procedure can be seen in Figure 2.6. The procedure is as follows:

1. Prior to use, the cell was connected to the inlet tap and terminal tap *via* Swagelok fittings, and the autoclave and connecting pipes were leak tested with nitrogen (to ~ 207 bar) to ensure all fittings were secured correctly and there were no leaks at the seals/joints. The inert gas was then vented from the terminal tap. After depressurisation, the autoclave body was charged with initiator V-70 (0.13g, 4.2×10^{-4} mol). Typically in the dispersion polymerisations described throughout this thesis, the ratio of monomer: stabiliser: initiator was 250:1:10.
2. The autoclave head was attached to the cell body and clamp sealed, using the pressure release pinwheel to tighten the clamp to its final position. The cell was then flushed with CO_2 (~3 bar) for 15 minutes.
3. The hydrocarbon stabiliser material (0.42g, 4.2×10^{-5} mol) being tested was dissolved in the monomer NVP (8.32g, 7.2×10^{-2} mol) and the solution was subjected to 3 freeze-pump-thaw cycles. The degassed

solution was withdrawn using a glass syringe and the mixture was injected into the cell through the safety valve. The pinwheel was placed back in the valve and tightened.

4. The autoclave was filled to ~55 bar with CO_2. The heater was then connected and set to the required temperature (35 °C) and the magnetically driven overhead stirrer was positioned on the autoclave head and set at 300 rpm.
5. Once the final temperature was attained and the system allowed to stabilise, the cell was gradually filled up to the final pressure (276 bar). The reaction proceeded for 48 h.
6. After 48 h, the heater was switched off at the mains and the cell cooled. The cell was vented slowly through the terminal tap into the fume hood, until atmospheric pressure was reached. The clamp was removed and the autoclave opened. Following successful dispersion polymerisation, the product was retrieved from the autoclave base as a dry, free flowing, white powder.

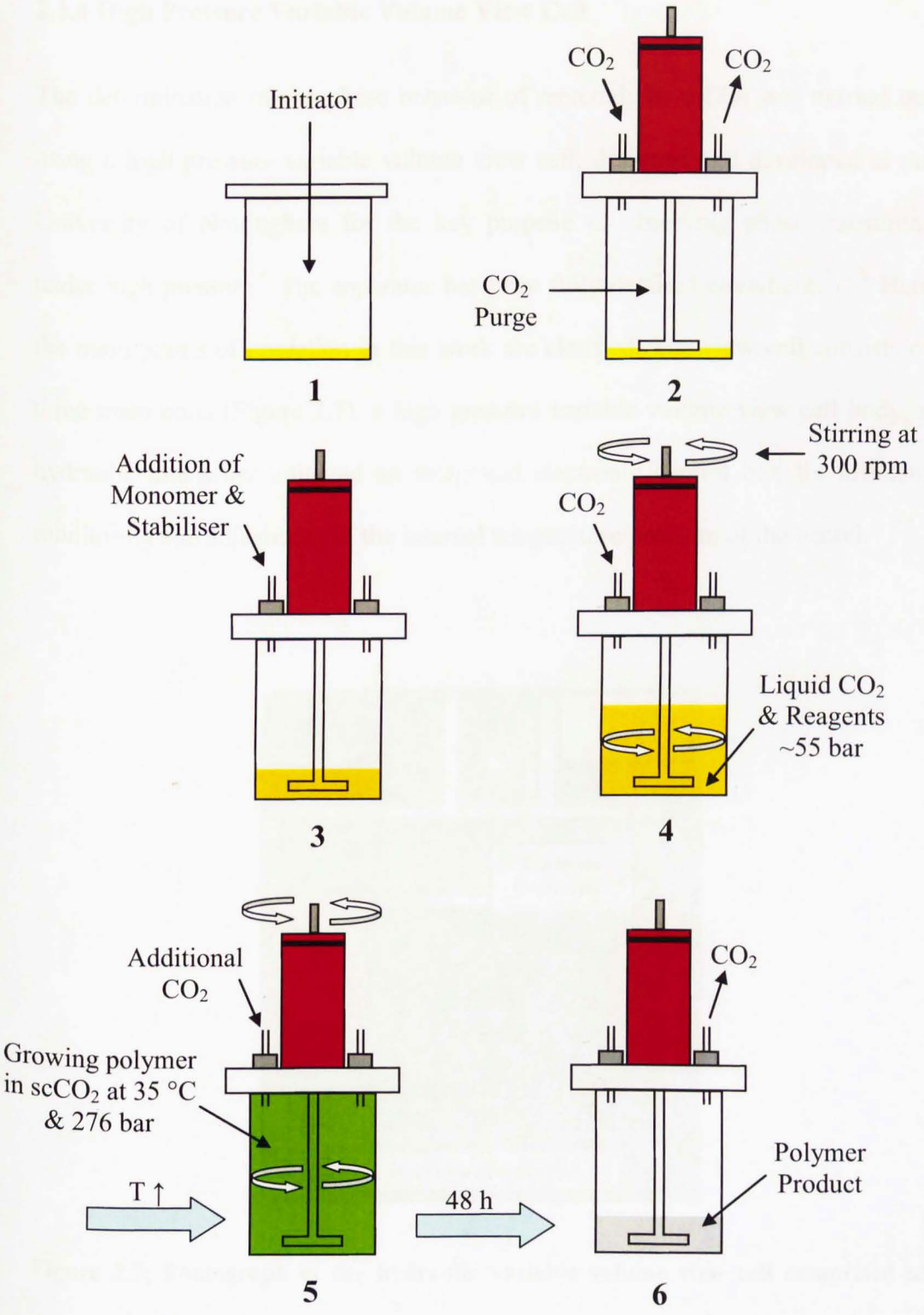


Figure 2.6: Schematic diagram illustrating the stepwise procedure for a typical dispersion polymerisation conducted in $scCO_2$.

2.1.4 High Pressure Variable Volume View Cell

The determination of the phase behavior of materials in $scCO_2$ was carried out using a high pressure variable volume view cell, designed and developed at the University of Nottingham for the key purpose of observing phase transitions under high pressure.[6] The apparatus has been fully detailed elsewhere.[4, 6, 7] Here the main points of operation in this work are clarified. The view cell consists of three main units (Figure 2.7): a high pressure variable volume view cell body, a hydraulic intensifier unit and an integrated electronic control box for efficient monitoring and adjustment of the internal temperature/pressure of the vessel.

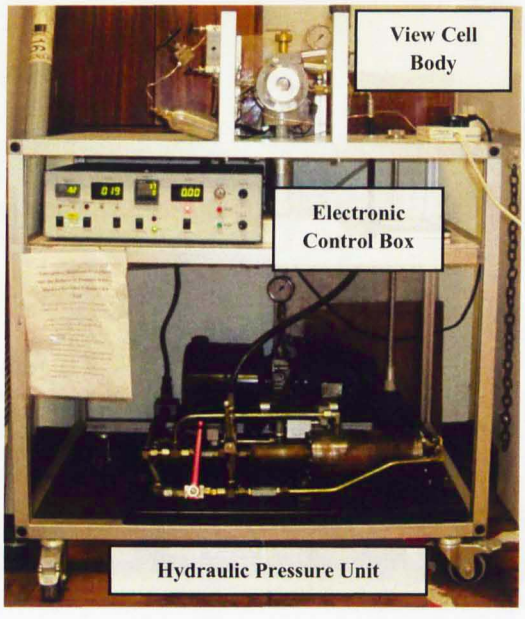


Figure 2.7: Photograph of the hydraulic variable volume view cell comprised of three key units.

The variable volume view cell adopts fundamental features present in the Mk III autoclave, with similar sealing, heating and stirring mechanisms. Six heating cartridges are slotted into cavities in the walls of the view cell body to deliver efficient heating to the cell. A magnetically coupled stirrer is positioned beneath the body of the view cell, which is used to rotate a magnetic flea inside the chamber. The main body has three main ports; one at the left for the inlet and outlet of CO_2, one at the right for a K-type thermocouple which protrudes into the main chamber for monitoring the internal temperature, and a third at the top for the safety valve/key (Figure 2.8).

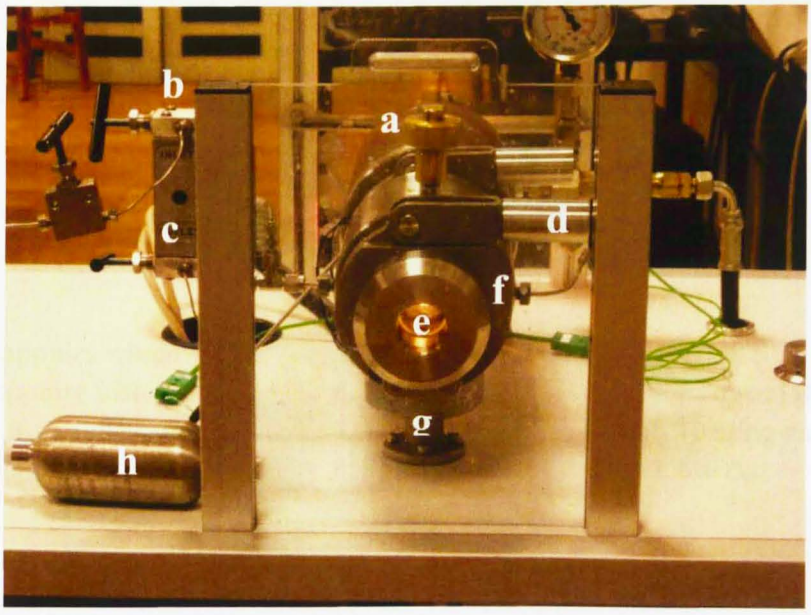
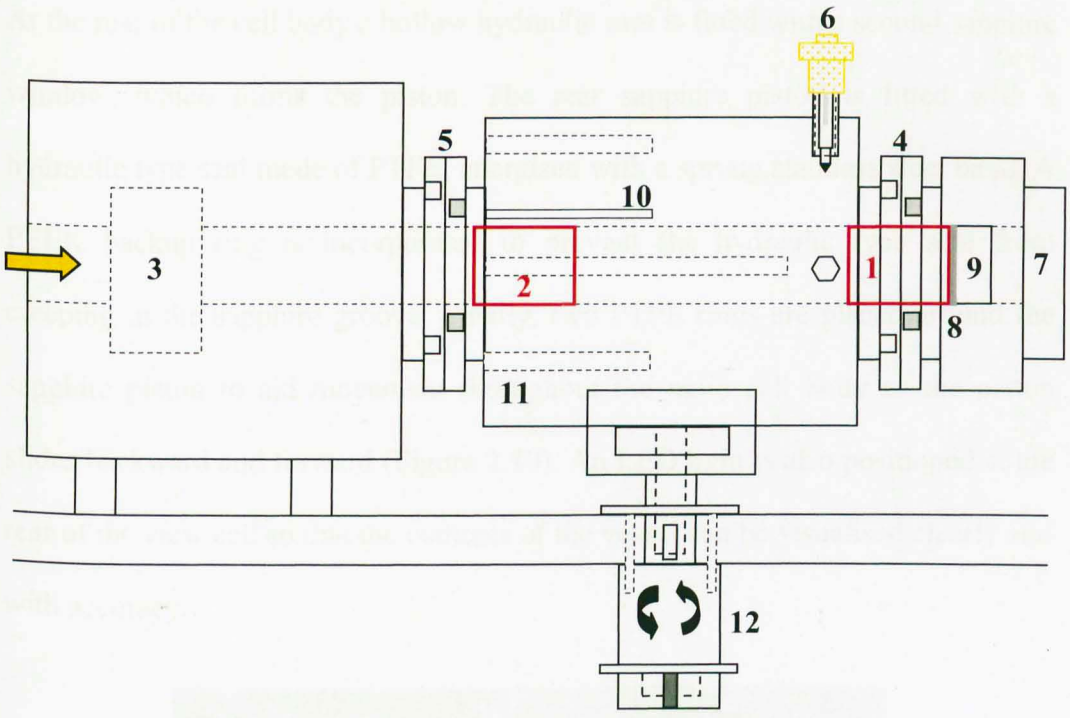


Figure 2.8: Photograph of front of view cell, which allows direct observation of phase transitions. (a) Safety valve; (b) CO_2 inlet; (c) CO_2 outlet; (d) Clamp; (e) Sapphire window (f) Internal thermocouple; (g) Magnetically coupled stirrer; (h) CO_2 bomb for delivery of gas to view cell.

The main body of the view cell is constructed of stainless steel and has a static sapphire window at the front, allowing for visualization of the phase behaviour (Figure 2.9).



1. Static sapphire window
2. Rear sapphire piston
3. Hollow hydraulic ram
4. Front clamp
5. Rear clamp
6. Safety valve
7. Window
8. Spacer
9. Teflon Seat
10. External thermocouple
11. Heating cartridges
12. Stirrer

Figure 2.9: Schematic of hydraulic variable volume view cell, allowing the internal volume of the cell to be increased/decreased through the hydraulic unit, subsequently adjusting pressure. Cell is lighted from behind to allow for visual observation.

The sapphire window sits on a Teflon seat in a stainless steel holder against an EPDM O-ring. Upon pressurising the cell, the sapphire window is forced against both the seat and the O-ring, creating an effective seal. A stainless steel spacer is also used in the window holder to adjust the volume of the vessel.

At the rear of the cell body a hollow hydraulic ram is fitted with a second sapphire window, which forms the piston. The rear sapphire piston is fitted with a hydraulic type seal made of PTFE, energised with a sprung stainless steel band. A PEEK backup ring is incorporated to prevent the hydraulic type seal from creeping in the sapphire groove. Finally, two PTFE rings are placed around the sapphire piston to aid movement throughout the main cell body as the piston slides backward and forward (Figure 2.10). An LED light is also positioned at the rear of the view cell so that the contents of the vessel can be visualised clearly and with accuracy.

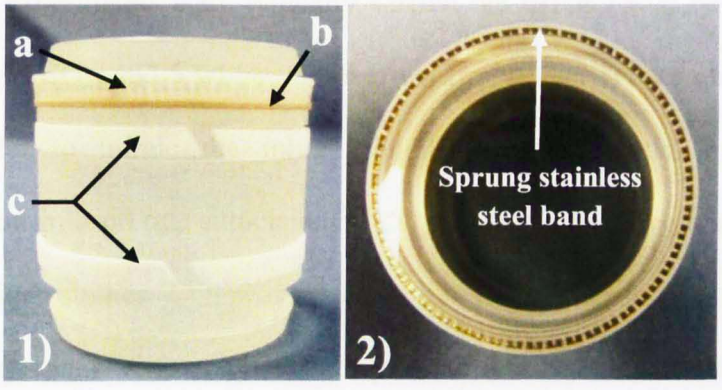


Figure 2.10: Sapphire piston and associated high pressure seals. (1) Image of rear sapphire window sealing system highlighting (a) stainless steel energised PTFE seal; (b) PEEK backup ring; (c) PTFE rings. (2) Overhead view of sprung stainless steel PTFE seal.

The piston is controlled by the hydraulics intensifier unit, which is able to deliver a smooth flow of hydraulic fluid into/out of the hollow ram. The hydraulic fluid displaces the position of the ram and in turn, the sapphire piston. This allows the internal volume of the cell to be increased and decreased *via* movement of the sapphire piston, resulting in a corresponding change in the internal pressure of the cell. Two switches are incorporated into the electronic control box to adjust hydraulic pressure as required.

2.1.5 Procedure for Determination of Phase Behaviour in $scCO_2$

The hydraulic variable volume view cell was employed for determination of phase behavior data for various synthesised stabiliser materials throughout this thesis.[4, 6]

Cloud point experiments were typically carried out using 15 wt % of monomer with respect to CO_2, and 5 wt % stabiliser w.r.t monomer. These quantities were used in order to mimic the initial conditions of a typical high pressure polymerisation in a 60 mL autoclave. A CO_2 loading of ~ 20 g was used in all phase behaviour studies. CO_2 was added to the view cell using a stainless steel CO_2 cylinder, which was weighed both prior to and after use to determine the weight of CO_2 in each experiment.

The procedure for a typical view cell experiment is shown schematically (Figure 2.11), and can be described as follows:

1. The stabiliser was dissolved in a specific amount of monomer and injected into the view cell through the safety needle valve port. CO_2 was added to the view cell through the inlet *via* a stainless steel bomb. The bomb was gently heated to aid CO_2 transfer. The bomb was disconnected once the cell was half filled with CO_2 (corresponding to ~20g). The exact weight of CO_2 added was calculated by weighing the bomb before and after addition.
2. The contents of the view cell were then stirred and the temperature was allowed to rise to the desired value (*e.g* 35 °C). The system was then allowed to equilibrate for 10 minutes. The sapphire piston was pushed forwards *via* the hydraulic system in order to increase the pressure by decreasing the internal volume. Once a sufficiently high pressure is reached, the stabiliser/monomer mixture will be completely dissolved and the light at the back of the cell will be completely visible.
3. The piston was then slowly moved back to decrease the internal pressure, and at a particular pressure the stabiliser started to precipitate out. This allows accurate recording of the pressure at which the polymer precipitates out of the continuous phase at a given termperature. This point can be defined as the cloud point. Cloud point measurements were taken from 35-75 °C and used to produce pressure-temperature phase diagrams.

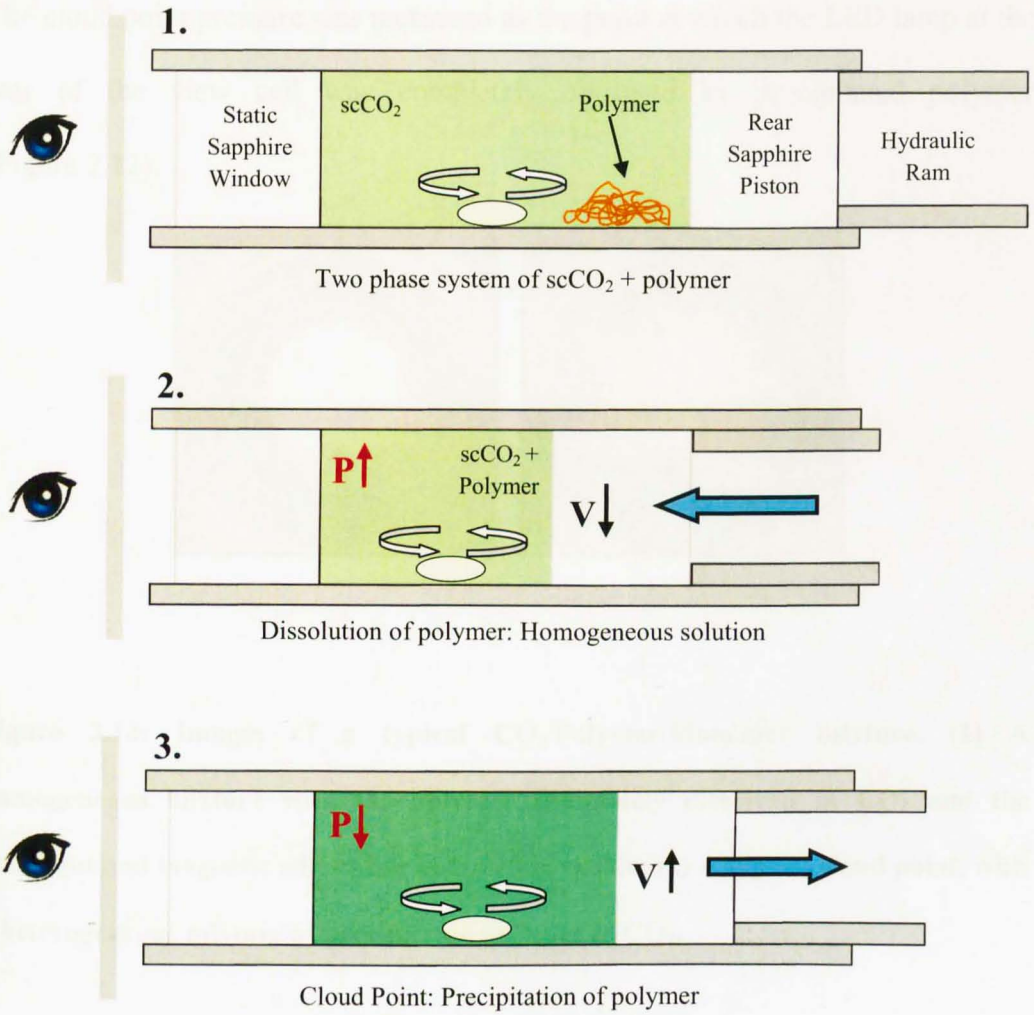


Figure 2.11: Schematic procedure for the high pressure variable volume view cell. (1) View cell is filled with $scCO_2$ and polymer as two separate phases. (2) The rear piston is moved forwards and cell volume decreases, increasing pressure and solubilising the polymer in the continuous phase. (3) The piston is moved backwards and the pressure is lowered until the cloud point pressure is reached.

The cloud point pressure was measured as the point at which the LED lamp at the rear of the view cell was completely obscured by precipitated polymer (Figure 2.12).

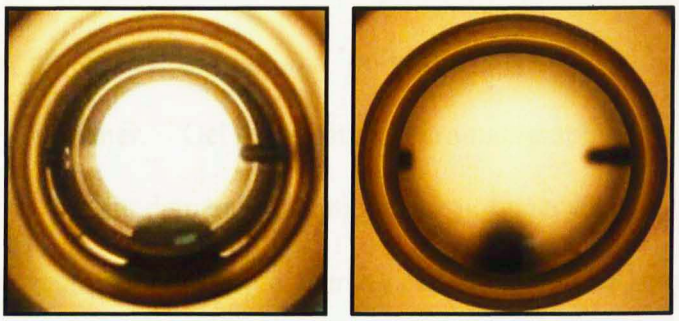


Figure 2.12: Images of a typical CO_2/Polymer/Monomer mixture. (1) A homogeneous mixture with the polymer completely dissolved in CO_2 and the backlight and magnetic stirrer bar completely visible; (2) A typical cloud point, with a heterogeneous mixture of precipitated polymer in CO_2.

All cloud point pressures in this thesis were taken three times and an average of these measurements was used, accurate to ±0.5-1.0 bar. Temperature of the system was controlled with a K-type thermocouple accurate to ±0.3 °C. The maximum safe working pressure of the view cell is 414 bar, so if a sample is insoluble below this pressure, no reading can be obtained.

2.2 Characterisation Techniques

2.2.1 Gel Permeation Chromatography (GPC)

Molecular weight and its distribution are key parameters in the characterisation of polymers. The molecular weight and polydispersity will affect the physical properties of a polymer. Gel permeation chromatography, or size exclusion chromatography, is a fundamental technique for polymer analysis, which allows both molecular weight and the polydispersity of a sample to be determined.[8-10]

Molecular weight and polydispersity of the hydrocarbon stabiliser samples within this thesis were determined using Gel Permeation Chromatography (PL-GPC 120, Polymer Labs) with differential refractometer detection. THF was employed as an eluent, with 2 columns (30 cm, PolarGel-M) in series calibrated against polystyrene standards and a flow rate of 1 mL min^{-1}. A PL-GPC 50 was employed for characterisation of poly(vinyl pyrrolidone) (PNVP) samples, using chloroform with 5 % triethylamine as the eluent, and calibration against PS standards.

2.2.2 Nuclear Magnetic Resonance (NMR)

^{1}H NMR is a technique widely applied in the chemical, structural and electronic study of molecules. NMR studies the magnetic nuclei of molecules by the alignment of the nuclei with a constant applied magnetic field, and the alignment is perturbed using an alternating external magnetic field. NMR allows a spectrum of resonance frequencies of the molecule to be generated which gives information

about the chemical structure.[11, 12] NMR is used throughout this work to probe the structure, composition ratio, conversion and molecular weight of polymers.

All ^1H NMR spectra were obtained using a Bruker DPX-300 (300 MHz) spectrometer, with $CDCl_3$ as the solvent. Analysis was carried out using MestRe-C software.

2.2.3 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) is primarily used to study the surface topology of solid samples. The method uses a focused high energy beam of electrons which illuminates the sample and scans line by line over its surface whilst held in a high vacuum.[13-15] In this thesis, SEM will be used extensively to characterise the polymer products obtained during dispersion polymerisation.

All SEM analysis was carried out using a JEOL 6060L V Variable pressure scanning electron microscope. Image analysis was performed with JEOL analysis software (version 6.57). Samples were prepared by placing the polymer sample on the surface of adhesive carbon tabs. These were attached to aluminium stubs, which were sputter coated with gold using a Balzers SCD 030 gold sputter coater. Mean particle diameter (D_n, μm) of the samples was determined by measuring ~100 particles from SEM data using ImageJ analysis software, and calculating a mean value from these results.

2.2.4 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) is a thermal analysis technique in which the difference in heat flow rate between a sample and a reference material is monitored whilst both are subjected to a controlled temperature programme.[16-18]

DSC is a useful analytical tool in the study of polymers, as it allows a number of properties to be obtained, such as melting temperature and glass transition temperature. The technique is used throughout this thesis to obtain information on the T_g of the synthesised stabiliser materials.

TA- Q2000 DSC (TA instruments) was employed for thermal analysis of the hydrocarbon stabilisers within this thesis. The DSC was calibrated with an indium standard and a heating/cooling rate of 10 °C/min was applied for all sample runs, with a nitrogen flow rate of 50 mL/minute, and a temperature range between 0 °C and 100 °C. Aluminum sample pans were employed with a sample mass of approximately 5 mg. The T_g was determined as the midpoint of the change in heat capacity during the second and third heating run for a given sample, and an average value from the two runs was taken.

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Chapter 3: Synthesis and Solubility of PVPi-based Stabilisers for $scCO_2$

This chapter describes the design and synthesis of hydrocarbon stabilisers using the monomer vinyl pivalate *via* RAFT/MADIX polymerisation. The chapter deals with the synthesis and characterisation of these materials, including detailed phase behaviour studies in $scCO_2$ using the high pressure variable volume view cell. The statistical copolymer stabilisers were synthesised from poly(vinyl acetate) (PVAc) and poly(vinyl pivalate) (PVPi) monomer units using RAFT/MADIX polymerisation.

A variety of stabilisers were synthesised and tested with different monomer ratios and molecular weights. In addition, the effect of PDI, co-monomer weight percentage, and the use of alternative monomers to VAc is briefly considered.

RAFT terminated PVPi-X homopolymer and PVAc-*s*-PVPi-X statistical copolymer stabilisers were tested for solubility in $scCO_2$ using the high pressure variable volume view cell and fully characterised using NMR, GPC and DSC.

3.1 Introduction

There have been a wide range of stabilisers designed for use in $scCO_2$. However, as described in Chapter 1, these stabilisers are predominantly fluorinated and siloxane based polymers. Bearing this is mind, there is a need for polymers with the ability to act as alternatives to the costly and potentially toxic stabilisers currently available. The work presented in this section aims to prepare a series of hydrocarbon polymers with significant CO_2-solubility and the design of these materials forms the foundation of the work presented in this thesis.

3.1.1 Stabilisers for $scCO_2$

Supercritical carbon dioxide ($scCO_2$) is an attractive alternative to conventional solvents for dispersion polymerisation because it is environmentally acceptable, inexpensive and leaves no solvent residues.[1-3] However, a perceived major drawback to the use of $scCO_2$ is the poor solubility of high molecular weight materials.[4-8] But this can be a distinct advantage for heterogeneous polymerisations, such as dispersion polymerisations. The major hurdle to overcome for any heterogeneous processing is the need for highly soluble dispersants or stabilisers that are commercially viable and environmentally acceptable.

Dispersion polymerisation employs a stabiliser material which will anchor to the surface of the growing polymer particles in the reaction medium. Polymeric stabilisers are required in dispersion polymerisations to produce a stable latex of

growing polymer particles and allow solubilisation of these particles in the continuous phase.[1, 9] The stabilisers surround the surface of the individual polymer particles and in doing so provide a method of solvation for the macromolecules within the solvent system. Stabilisers tend to be amphiphilic and consist of two components; a polymer-philic anchor group and a CO_2-philic tail.

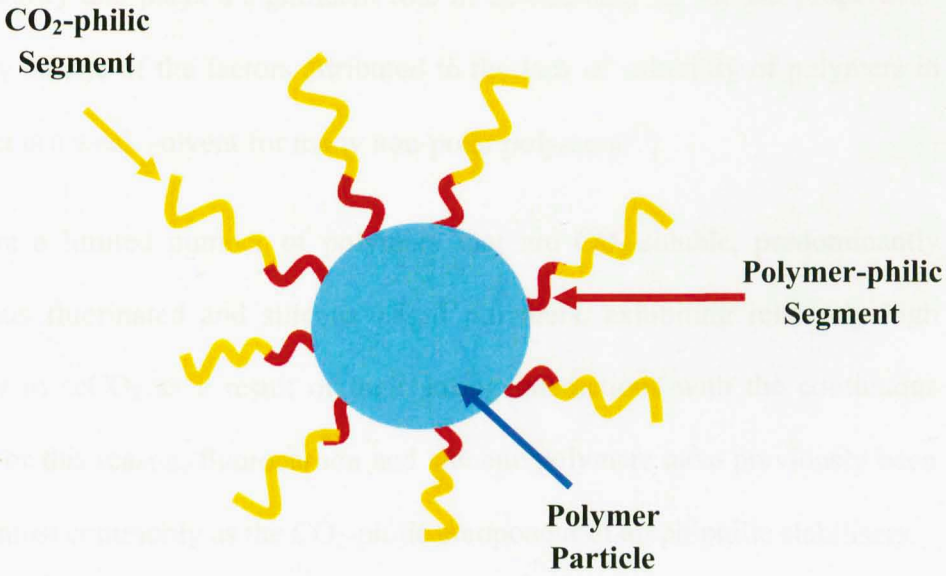

Figure 3.1: Schematic of a growing polymer particle in $scCO_2$, with surfactant molecules surrounding the surface and providing stabilisation.

A number of materials have been used successfully as steric stabilisers in $scCO_2$ based free radical polymerisation systems. However, many stabilisers are designed for organic or aqueous continuous phases and have limited solubility in CO_2 because of the properties of carbon dioxide as a solvent.[4] As previously

mentioned, carbon dioxide is a weak solvent for the majority of high molecular weight compounds. Supercritical CO_2 can be described as a non-polar, hydrophobic solvent, comparable to n-hexane, but actually closer to that of fluorocarbon solvents.[10] The main difference between CO_2 and hexane solvation strength involves the Lewis acid/base properties. CO_2 is non-polar with no permanent dipole, but possesses a large quadrupole moment, which results in a small polarity and plays a significant role in determining its solvent properties.[6] This may be one of the factors attributed to the lack of solubility of polymers in CO_2, as it is a weak solvent for many non-polar polymers.[11]

There are a limited number of polymers that are CO_2-soluble, predominantly amorphous fluorinated and silicone based polymers, exhibiting relatively high solubility in $scCO_2$ as a result of their strong interactions with the continuous phase. For this reason, fluorocarbon and silicone polymers have previously been adopted most commonly as the CO_2-philic component of amphiphilic stabilisers.

As described in Chapter 1, over the last two decades a range of fluorinated stabilisers, such as Krytox 157-FSL and poly(1, 1-dihydroperfluorooctyl acrylate) (PFOA), have been successfully used in dispersion polymerisations in $scCO_2$.[12-15] More recently silicones such as poly(dimethylsiloxane) (PDMS), have also shown promise as successful stabilisers for methyl methacrylate (MMA) polymerisations in $scCO_2$.[16, 17] To date a range of fluorinated and silicone homopolymer, block copolymer and graft copolymer structures have been employed in dispersion polymerisations.[3, 15, 18-22] However, the need to develop an alternative,

hydrocarbon-based stabiliser to replace these materials is becoming a key issue in polymer synthesis in CO_2.

3.1.2 Solubility of Non-Fluorous Polymers in CO_2

The use of fluorocarbons and silicones in CO_2 has disadvantages, namely their potential toxicity and high cost. In addition, such stabilisers are often retained in the final product and adhere to the surface, affecting the properties of the material. The lack of inexpensive, alternative stabilisers is perhaps one of the key reasons why $scCO_2$ processes have not been widely commercially adopted. Recently there has been an increasing drive to discover new CO_2 soluble hydrocarbon materials for use in $scCO_2$, which are free of silicone and fluorine containing components. This has led to a development in the understanding of the phase behaviour of hydrocarbon polymers in CO_2.

Significant research has focused on identifying polymers which are soluble in CO_2 at moderate temperatures and pressures. Bray *et al.* recently reported the development of polyester libraries to aid in the understanding of structure-solubility relationships between polymers and CO_2.[23] Whilst the linear alkyl polyesters were not significantly soluble in $scCO_2$, branching in the diacid or diol moiety imparted a significant increase in solubility, and branching with acyl chains strongly enhanced solubility. This led to the conclusion that further development of highly branched polyesters could potentially provide polymers with high CO_2-philicity.

Beckman and coworkers reported the development of poly(ether-carbonate) (PEC) copolymers synthesised from propylene oxide (PO) and CO_2, which were able to act as efficient, non-fluorous CO_2-philes and readily dissolved at low CO_2 pressures (Figure 3.2).[24] A PO/CO_2 copolymer of 250 repeat units with 15.4 % carbonate was found to be significantly more soluble than a comparable fluoroether. In addition, a PO homopolymer of equivalent chain length was found to be insoluble within the limits of the system (500 bar). The favourable solubility of the PEC materials was attributed to the main chain carbonate linkage, which acted to improve the enthalpy of mixing through the presence of a carbonyl group, increasing the degree of flexibility, and consequently the entropy of mixing. The authors proposed that the miscibility pressures of a copolymer exhibiting the optimal content of two monomers will be more soluble than either of the corresponding homopolymers. To demonstrate this, a series of polymers with a chain length of 25 repeat units was compared, and a 100 % carbonate polymer was found to be insoluble. However, a 40 % PEC copolymer exhibited lower cloud point pressures than a 100 % PO homopolymer, confirming the improved solubility of a copolymer structure.

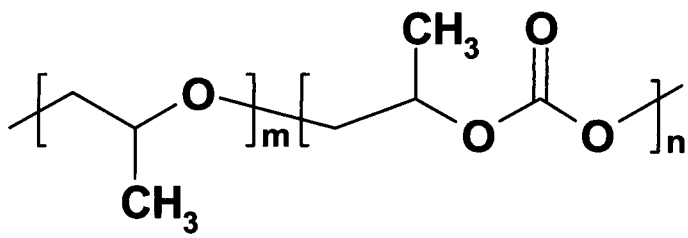

Figure 3.2: Poly(ether carbonate) developed by Beckman and coworkers.[24]

Cooper and coworkers also produced PEC and PEE copolymers as potential inexpensive hydrocarbon materials, using the method of step growth polymerisation.[25] The polymers were found to be soluble in CO_2, but only at modest molecular weights of <10 kg/mol. Drohmann and Beckman also carried out research on a series of polymers including poly(ethylene glycol)s, poly(propylene glycol)s, copolymers of ethylene oxide and propylene oxide, and poly(ethyl vinyl ether).[26] It was identified that the presence of an accessible ether oxygen enhanced CO_2-solubility through Lewis base-Lewis acid interactions. The solubility of these materials was found to be influenced by a range of factors including molecular weight and end-group of the polymer. Sugar acetate structures have also been proposed by Wallen *et al.* as potential CO_2-philes, with the incorporation of acetate groups within the peracylated sugar structure providing a route to carbohydrates with significant miscibility pressures in CO_2.[27]

Recently, much attention has been given to the observed high solubility of hydrocarbon polymers such as poly(vinyl acetate) (PVAc) which contain carbonyl and acetate groups.[25, 28-31] These materials have been recognised as having appreciable solubility in CO_2 when compared to other hydrocarbon polymers. The carbonyl group of PVAc is proposed to be involved in favourable interactions with CO_2; the electron-donating oxygen group of the carbonyl promoting Lewis acid-base interactions with the carbon of CO_2.[32] Carbon dioxide is a weak Lewis acid and as such it has the potential to interact with functional groups such as ethers, esters and acetates (Lewis bases). Kazarian and coworkers confirmed this interaction using FT-IR spectroscopic studies to investigate the splitting of the

CO_2 bending mode (υ_2).[33] Further to this, Raveendran *et al.* carried out research involving a comprehensive spectroscopic study of CO_2-carbonyl complexes, verifying this Lewis acid-base interaction. In addition, NMR and vibrational spectra gave evidence to suggest that there is an additional weak, cooperative intermolecular interaction between the -CH of the hydrogen atom attached to the carbonyl group, and the oxygen of the CO_2.[34]

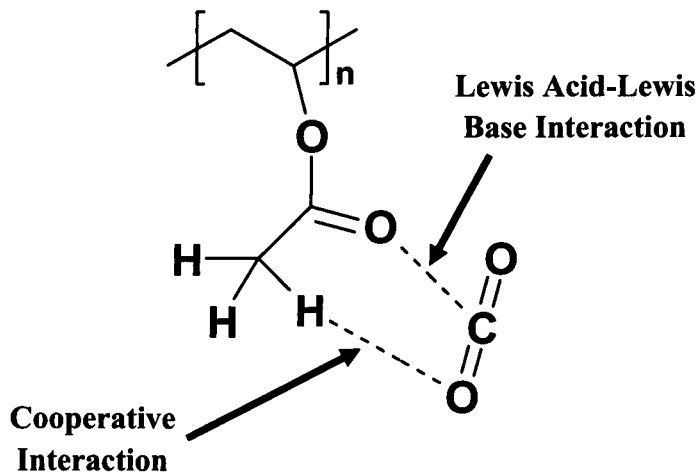

Figure 3.3: Lewis acid-base interaction between PVAc and CO_2.

It is the interaction of the acetate functionality with CO_2, and the accessibility of these groups, which results in the significant solubility of PVAc. Poly(methacrylate) (PMA) has a very similar structure to PVAc, yet is much less soluble. PMA was observed by Shen *et al.* to have much lower solubility than PVAc, with a cloud point pressure of 2250 and 640 bar respectively, despite the

fact that the repeat unit is comprised of the same functional groups, in slightly different positions.[30] This distinct shift in solubility is probably related to the fact that the carbonyl group is positioned closer to the backbone of the polymer in PMA, and so is restricted in terms of rotational freedom. Conversely, PVAc has an ether linkage separating the acetate group from the backbone, and the acetate group can rotate freely about this bond, making it more accessible for interaction with CO_2.

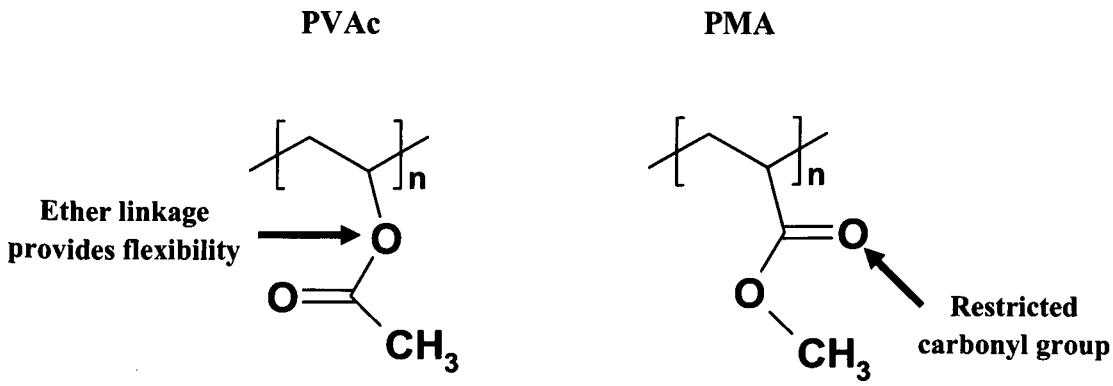

Figure 3.4: The structures of PVAc and PMA respectively. The ether linkage of PVAc provides a means by which the acetate group can freely rotate to interact with CO_2.

The highly CO_2-philic nature of PVAc compared to other hydrocarbon polymers has led to an increased interest in the design of PVAc-based materials which have improved solubility. Howdle and coworkers reported the synthesis of a series of poly(vinyl alkanoate) copolymers using xanthate mediated RAFT polymerisation

to control the molecular weight and PDI. Both homopolymers and copolymers of vinyl acetate, vinyl butyrate and vinyl octanoate monomers were synthesised.[35]

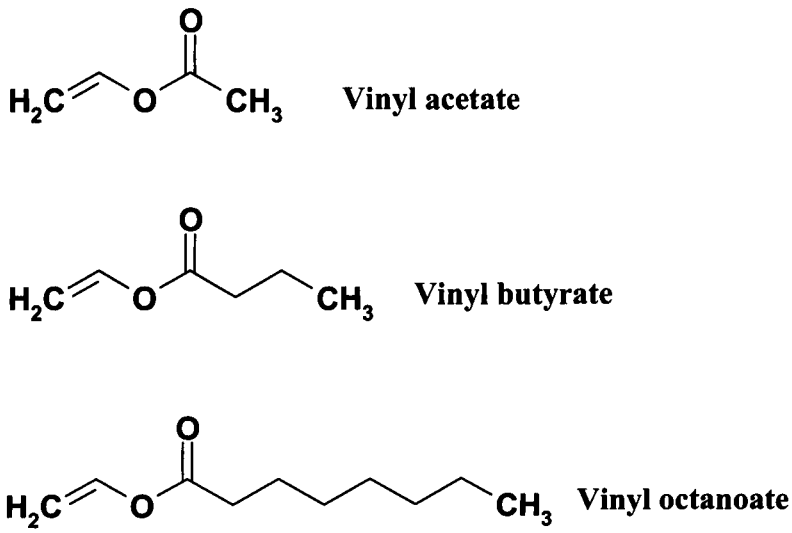

Figure 3.5: Vinyl monomers VAc, VBu and VOc used for the synthesis of poly(vinyl alkanoate) stabilisers.

The results suggested that solubility was improved by increasing the side chain length of the polymeric stabiliser *via* addition of VBu, to incorporate additional flexibility and increased free volume. However, as the alkyl chain was increased further, and copolymers of VAc and VOc were synthesised, interactions between CO_2 and the hydrocarbon chains became less favourable. It was proposed that the octanoate tail enhances the flexibility of the side chain, and also increases the free

volume, which improves solubility of the polymer in CO_2, but this increased flexibility cannot overcome the unfavourable energetics of the interactions between the alkyl chain and CO_2.

These results confirm previous observations from similar studies investigating the impact of alkyl chain length in $scCO_2$.[36, 37] McHugh *et al.*, for example, observed for a series of poly(acrylates) with varying side chain lengths that the polymers with longer side chains were less soluble.[36] At the temperatures employed in the study, polar interactions were proposed to have a significant impact. As the alkyl tail of the poly(acrylate) was increased, the effective polarity of the polymer also decreased, which resulted in reduced polymer solubility. This led to poorer solubility compared to the poly(acrylates) of smaller hydrocarbon side chain lengths. Increased solubility was observed if the chain was at least partially fluorinated, and had partial polarity.

The synthesis of a range of CO_2-soluble hydrocarbon alternating copolymers of vinyl acetate and dibutyl maleate has also been reported.[38] Phase behaviour measurements of the PVAc-*alt*-PDBM polymers showed promising solubility, much higher than that of PVAc homopolymer and approaching that of PFPE and PDMS-mMA, which was attributed to the increase in free volume of the polymer upon incorporation of the highly branched DBM monomer.

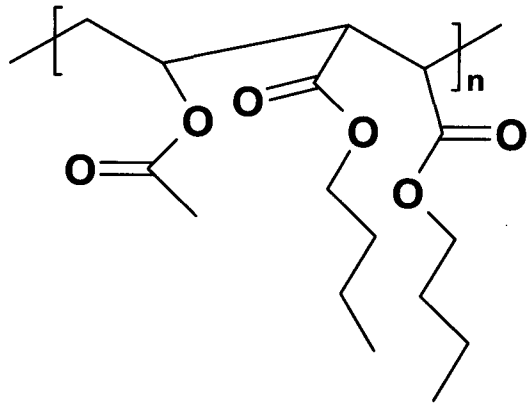

Figure 3.6: CO_2-philic PVAc-alt-PDBM copolymers.[38]

All of these materials highlight routes to new hydrocarbon surfactants *via* the design of polymers with improved solubility in CO_2. However, currently there are only a limited number of polymers which have been found to possess significant CO_2-solubility, and there is still a need to design CO_2-philic polymers for application in synthesis and processing, which approach the solubility of fluorine and silicone containing analogues.

3.1.3 Design of Hydrocarbon Stabilisers

The design of novel, highly CO_2-soluble stabilisers that overcome the current limitation requiring use of fluorinated or siloxane based materials for synthesis and processing is a key challenge for dispersion polymerisation in $scCO_2$. In light of this, and based upon previous observations, Beckman *et al.* developed a series of heuristics outlining the requirements a material must meet to act as a CO_2-soluble stabiliser.[39]

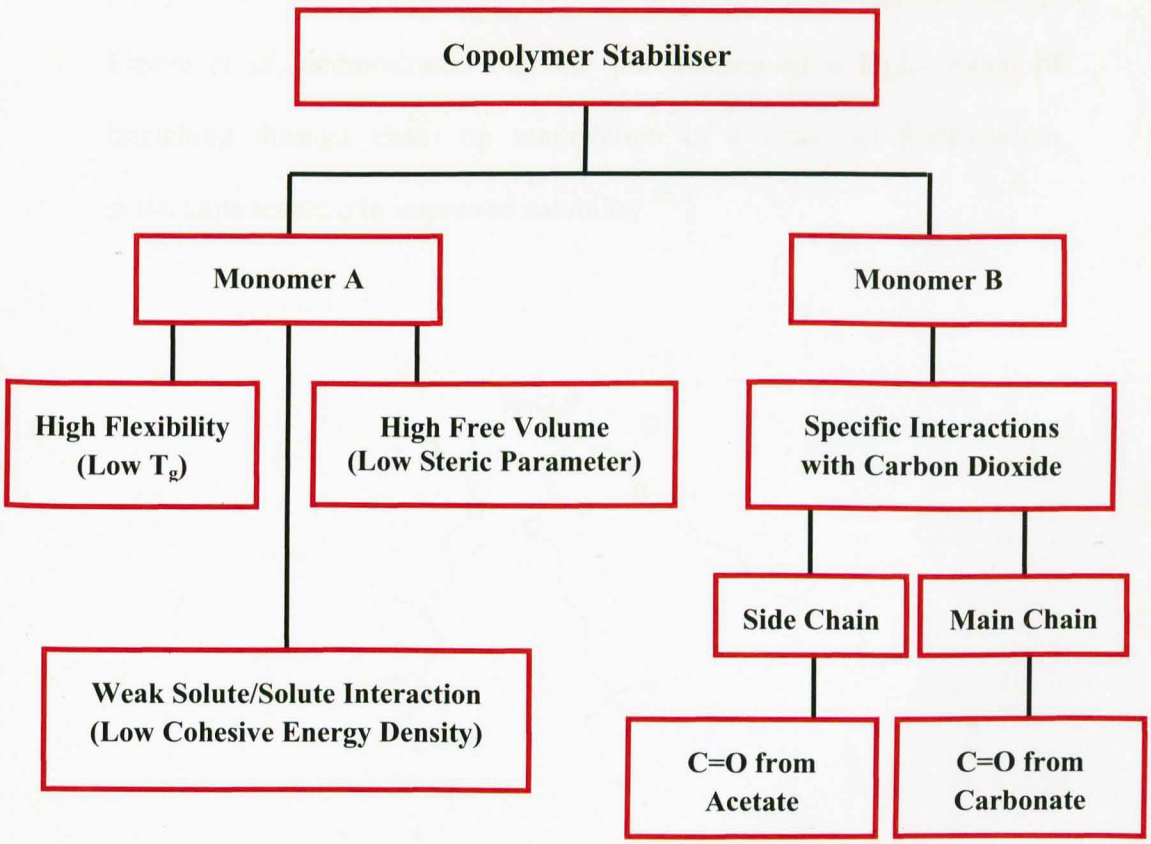

Figure 3.7: Stabiliser design parameters proposed by Beckman *et al.* for synthesis of CO_2-soluble hydrocarbon material.[39]

The results suggest that a hydrocarbon stabiliser should possess:

(1) **High flexibility *e.g.* ether oxygen linkages.** The incorporation of increasing flexibility through the use of longer side chains or flexible linkages will act to increase the free volume of the polymer, often resulting in a subsequent decrease in the glass transition temperature and enhanced entropy of mixing, improving solubility.

(2) **High free volume *e.g.* highly branched structures.** Increasing the free volume of a polymer *via* the incorporation of highly branched or flexible groups will act to increase the free volume and improve CO_2-solubility. Eastoe *et al.* demonstrated that the introduction of a high degree of branching through chain tip methylation of a series of hydrocarbon surfactants resulted in improved solubility.[40, 41]

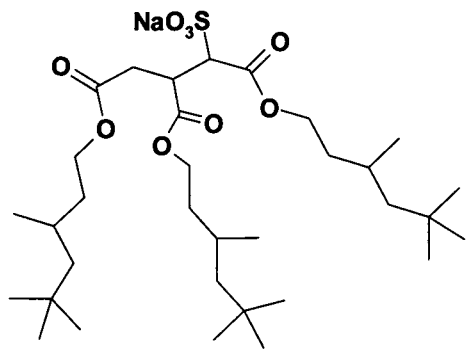

Figure 3.8: Anionic surfactant TC 4, triple chain analogue of AOT surfactant for use in $scCO_2$.[41]

(3) **Functional groups available to interact with carbon dioxide *e.g.* carbonyl/acetate groups.** The presence of oxygen containing functional groups such as carbonyls will provide a specific interaction with CO_2. Such groups will also adjust the acidity of neighbouring protons, and will not significantly strengthen the self interactions of the solute.[42]

(4) **Weak solute/solute interactions.** The material should have a weak self-interaction and possess a low cohesive energy density, which results in low surface tension and a smaller barrier to dissolution. O'Neill *et al.* have proposed that the key characteristic a material should possess to exhibit CO_2-philicity is a weak self-interaction, as known interactions between CO_2 and many CO_2-soluble polymer materials are relatively weak themselves.[5] Weak self-interaction is an attribute of fluorinated and silicone polymers and contributes to their high solubility in $scCO_2$.

Additionally, research on CO_2-philic materials has also highlighted potentially unfavourable features which, when incorporated into a material, will have a negative impact on solubility in CO_2. Enick *et al.* reported the development of a series of seven hydrocarbon polymers containing tertiary amine groups in either the backbone or the side chain.[43]

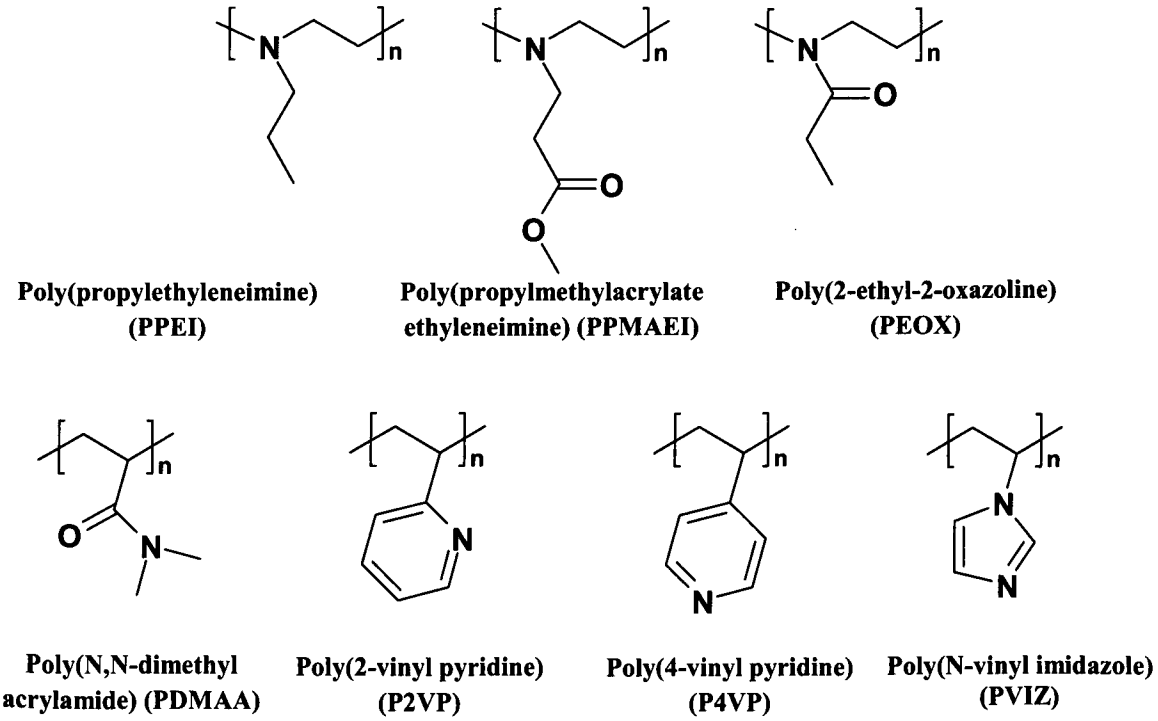

Figure 3.9: Structures of the nitrogen-containing hydrocarbon polymers tested by Enick *et al.*[43]

All of these polymers were found to be insoluble in CO_2, despite the CO_2-philic nature of the amine component. *Ab initio* calculations suggested that self interactions between the amine groups were energetically more favourable than CO_2-amine interactions, resulting in this reduced solubility. Allyl containing polymers, which possess a $-CH_2-$ spacer between the backbone and pendant group, have also been found to decrease solubility.[28]

As can be seen from the proposed guidelines in Figure 3.7, ideally a CO_2-philic polymer should be comprised of a copolymer of monomers M_1 and M_2. M_1

should generally contribute a high free volume, flexibility and weak self-interaction between the solute, often resulting in a low T_g and steric parameter (σ). The steric parameter gives an indication of chain flexibility and is a measure of the chain extension of the polymer in solution relative to the freely rotating chain. A lower σ indicates greater flexibility and entropy of mixing, thus improved solubility. M_2 should incorporate a means of interacting directly with CO_2, to provide specific solute/solvent interactions, in the form of Lewis bases such as carbonyls and acetates.

Interactions between M_1 and M_2 should be enthalpically unfavourable to promote dissolution in CO_2. The polymer should also be a copolymer structure, as a homopolymer of either M_1 or M_2 will only optimise part of the free energy. It is also important to find a suitable balance between the two monomers, optimising both the enthalpy of mixing and the entropy of mixing.

Despite extensive research and findings on designing CO_2-soluble hydrocarbon materials, it remains difficult to predict the solubility of a material in CO_2, and characteristics such as a low T_g or the presence of carbonyl groups will not always have as significant an impact on the solubility as expected. One example is that of poly(methylene acetate), which has a very high melting point and is reported to be insoluble in CO_2, despite having a higher degree of acetylation than PVAc.[31]

However, such guidelines serve as a basis for identifying materials with potential CO_2-solubility, by designing polymeric materials which combine all of these basic requirements and optimise dissolution in CO_2.

3.2 Experimental

3.2.1 Materials

Deuterated chloroform, potassium ethyl xanthate, ethyl 2-bromopropionate, magnesium sulfate, aluminium oxide, and HPLC grade tetrahydrofuran were acquired from Sigma Aldrich and were used as received. Monomers vinyl acetate (VAc) (99%) and vinyl pivalate (VPi) (99 %) were purchased from Sigma Aldrich. All monomers were stored at 3-4 °C and purified prior to use by passing through a column of activated aluminium oxide, and subsequently degassing *via* three freeze-pump-thaw cycles. The initiator 2, 2'-azobis(isobutyronitrile) (AIBN) was obtained from Acros and purified by recrystallisation twice from cold methanol. Poly(dimethyl siloxane mono methyl methacrylate) (10000 g mol^{-1}) was purchased from Itochu Chemicals Ltd. and used without further purification. Dry CO_2 (99.99%) and Nitrogen (99.99 %) were purchased from BOC.

3.2.2 Polymer Characterisation

Molecular weight and polydispersity of the hydrocarbon stabiliser samples were determined using Gel Permeation Chromatography (PL-GPC 120, Polymer Labs) with differential refractometer detection. THF was employed as an eluent, with 2 columns (30 cm, PolarGel-M) in series calibrated against polystyrene standards. Differential Scanning Calorimetry (DSC) analysis was obtained using a DSC Q2000 for thermal analysis. Measurements were run at 10 °C/min with a nitrogen

flow rate of 50 mL/min, and a temperature range between 0 °C and 100 °C. Determination of the composition ratios for the statistical copolymers, and the monomer conversion for all polymers, was calculated from the relevant peaks of the ^1H NMR spectra recorded using a Bruker DPX-300 Spectrometer in $CDCl_3$.

3.2.3 Synthesis and Polymerisations

3.2.3.1 Xanthate X1 Synthesis

All stabilisers synthesised throughout this thesis were prepared in a controlled manner *via* RAFT polymerisation. The synthesis of the xanthate *O-ethyl-s-(1-ethoxycarbonyl)ethyl dithiocarbonate* employed in the RAFT/MADIX polymerisation reactions is outlined in Figure 3.10 and adopted from the literature.[44]

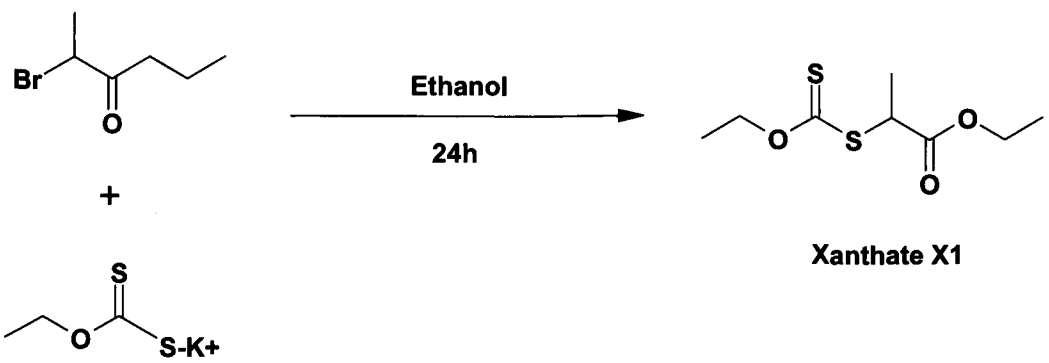

Figure 3.10: Xanthate X1 synthesis.

Xanthate X1 Synthesis: Ethyl 2-bromopropionate (11.12 g, 0.06 mol) was dissolved in ethanol (100 mL) in a 250 mL round bottomed flask. Potassium ethyl xanthate (10.86 g, 0.07 mol) was added to the solution over a period of 0.5 h. The solution was then degassed thoroughly with nitrogen and stirred at room temperature for 24 h. The resultant mixture was then filtered and the solution collected. The solvent was removed under reduced pressure to give a yellow liquid. The product was extracted in dichloromethane (100 mL) and washed with water (3 x 75 mL) using a separating funnel, dried with $MgSO_4$ and filtered. The solvent was then evaporated under reduced pressure and vacuum dried at room temperature for 24 h. The product obtained was a clear, yellow liquid. Yield= (87%). ^{1}H NMR ($CDCl_3$): δ = 4.65 (q, 2H), 4.39 (q, 1H), 4.22, (q, 2H), 1.58 (d, 3H), 1.42 (t, 3H), 1.28 (t, 3H). ^{13}C NMR ($CDCl_3$): δ = 212.0, 171.3, 70.2, 61.8, 47.2, 16.9, 14.1, 13.7.

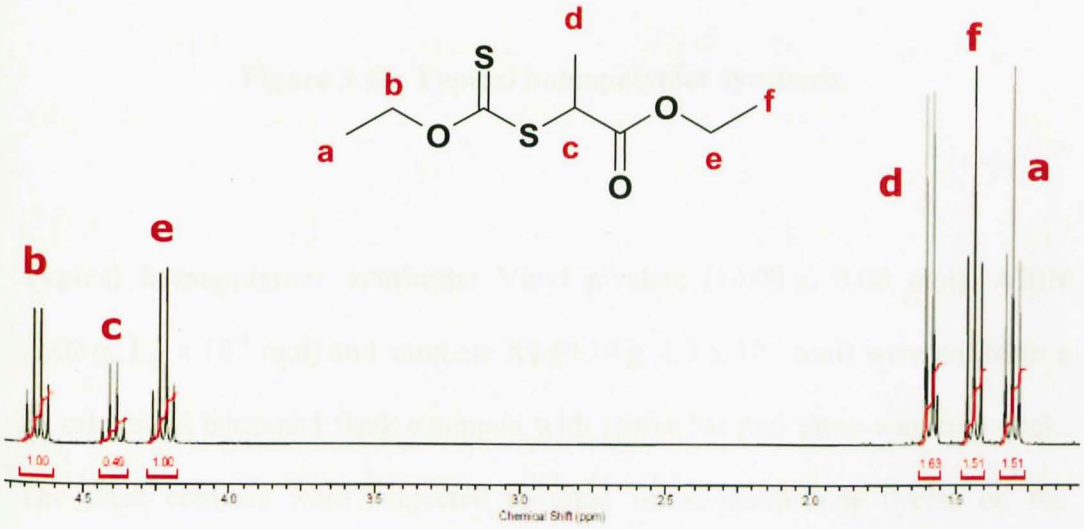

Figure 3.11: ^{1}H NMR of xanthate O-ethyl-*s*-(1-ethoxycarbonyl) ethyl dithiocarbonate (X1).

3.2.3.2 Homopolymer Synthesis

Homopolymers of the vinyl alkanoates were synthesised *via* a free radical RAFT/MADIX polymerisation method. The polymerisations were carried out in bulk using the xanthate X1 as a RAFT agent. A typical homopolymer synthesis is described in Figure 3.12.

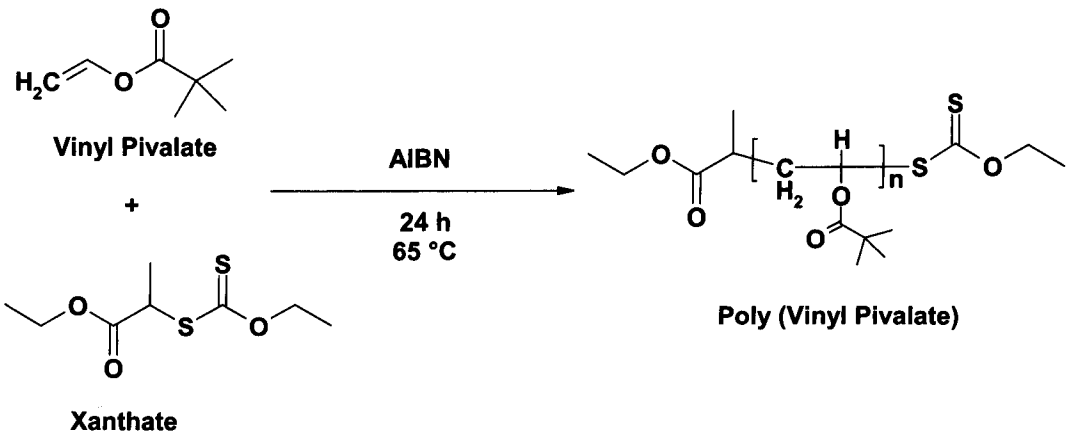

Figure 3.12: Typical homopolymer synthesis.

Typical homopolymer synthesis: Vinyl pivalate (10.00 g, 0.08 mol), AIBN (0.02 g, 1.3 x 10^{-4} mol) and xanthate X1 (0.29 g, 1.3 x 10^{-3} mol) were added to a 50 mL round bottomed flask equipped with stirrer bar and three-way stop cock. The flask contents were subjected to three freeze-pump-thaw cycles on the Schlenk line and charged with an inert gas. The reaction flask was immersed in an oil bath at 65 °C for 24 h. The poly(vinyl pivalate) polymer product was purified

via precipitation into a mixture of ice cold methanol: water (4:1). The final product was filtered, dried overnight on the vacuum line, and collected as a white powder. Typical M_n: 10.0 kg/mol, PDI: 1.33, Conversion: 85% (Table 3.1, entry 3).

Theoretical molecular weights and subsequently the ratio of monomer, initiator and AIBN to be used were determined using equation 3.1.[45]

$$M_{n,th} = \frac{[M]_0 - [M]_t}{[RAFT]_0} m_M + m_{RAFT}$$

Equation 3.1: Prediction of theoretical molecular weight ($M_{n,th}$) of polymer synthesised in RAFT polymerisation where $[M]_0$ is the initial concentration of the monomer, $[M]_t$ is the concentration at time t, $[RAFT]_0$ is the initial concentration of the RAFT agent employed, m_M is the molecular weight of the monomer and m_{RAFT} is the molecular weight of the RAFT agent.

3.2.3.3 Statistical Copolymer Synthesis

Statistical copolymers were also synthesised using the RAFT polymerisation technique.

Typical statistical copolymer synthesis: Vinyl acetate (3.73 g, 0.036 mol), vinyl pivalate (4.67 g, 3.6 x 10^{-2} mol), xanthate (0.13 g, 5.7 x 10^{-4} mol), AIBN (0.009 g, 5.7 x 10^{-5} mol) and dry toluene (5 mL) were added to a 50 mL round bottomed flask equipped with stirrer bar and three-way stop cock. The flask was then thoroughly degassed using three freeze-pump-thaw cycles. The flask was immersed in an oil bath at 65 °C for 48 h. The polymer product was purified *via* precipitation into a mixture of ice cold methanol: water (4:1). The mixture was filtered and the solid product dried in the oven. Typical M_n: 10.3 kg/mol, PDI: 1.44, Ratio: 24:76, Conversion: 63% (Table 3.2, entry 3).

3.2.3.Free Radical Copolymerisation

Free radical copolymers of VAc and VPi were synthesised to yield a PVPi-based copolymer with no xanthate functionality present. The proportion of AIBN was varied (2-6 wt %) in order to afford some control over the molecular weight of the final polymer product.

Typical Free Radical Copolymerisation: Vinyl pivalate (6.0 g, 4.5 x 10^{-2} mol), vinyl acetate (4.0 g, 4.5 x 10^{-2} mol), and AIBN (0.4 g, 2.4 x 10^{-3} mol) in toluene (5 mL) were added to a 50 mL round bottomed flask equipped with stirrer bar and the vessel sealed. The flask contents were degassed for ~ 30 mins and charged with an inert gas. The reaction flask was immersed in an oil bath at 65 °C for 24 h. The polymer product was purified *via* precipitation into methanol: water (4:1). The final product was filtered and vacuum dried. Typical M_n: 10.0 kg/mol, PDI: 2.05, Ratio: 29:71 Conversion: 86% (Table 3.8, entry 2).

3.2.4 Phase Behaviour Measurements

Phase behaviour measurements for both the homopolymers and statistical copolymers were determined using the high pressure variable volume view cell procedure as outlined in Chapter 2, section 2.2.2.[46, 47] All cloud point measurements were determined in a CO_2/NVP mixture. Once the desired quantities of CO_2, monomer and stabiliser were added, the volume of the cell was decreased to a point where a one phase mixture was obtained. The volume was then gradually increased, decreasing the pressure and density of the CO_2 phase, until the cloud point pressure was reached and the stabiliser precipitated out. All cloud points were repeated three times and an average of these values taken. Cloud point measurements were recorded from 35-75 °C.

3.3 Results and Discussion

3.3.1 Hydrocarbon Stabiliser Synthesis

The aim of this chapter was to identify a series of CO_2-soluble polymer materials which could find application as surfactants in dispersion polymerisations in $scCO_2$. Research in this area has previously been carried out in the group, and poly (vinyl alkanoate) random copolymers were identified as being particularly successful as hydrocarbon materials for dispersion polymerisations in $scCO_2$.[35, 38]

Vinyl pivalate (VPi) was identified as a potential monomer for incorporation as it has a structure similar to that of VAc, but possesses a tertiary butyl group in place of the methyl group of vinyl acetate. VPi has the potential to act favourably as a hydrocarbon stabiliser and have good solubility in $scCO_2$ due to the presence of this tertiary butyl group (Figure 3.13).

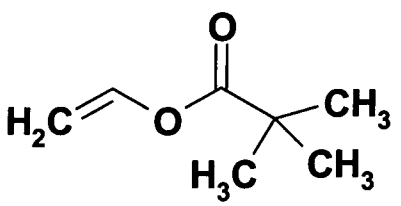

Figure 3.13: Vinyl pivalate monomer structure.

The presence of a bulky substituent in polymer systems will disrupt the regularity in the chain packing of polymers and results in increased spacing/free volume between the chains. This lowers the solubility parameter and increases solubility

in the reaction medium. In the case of VPi, the additional tertiary butyl group should in theory act to increase the solubility of the stabiliser material, compared to that of VAc.

Following the guidelines proposed by Beckman *et al.* (Figure 3.7), a copolymer of VAc and VPi has the potential to satisfy all the requirements for a CO_2-soluble material. Both VPi and VAc will impart a means of direct interaction with CO_2, in the form of a carbonyl group. The VPi units will act to provide an increased free volume between the polymer chains, and finally VAc will incorporate flexibility into the structure.

The molecular weight of a polymer will have an impact on the solubility and stabilising ability of the material in $scCO_2$. RAFT polymerisation has previously been employed as a means of both controlling the molecular weight of the polymeric surfactants, and providing a polymer end group suitable for acting as the polymer-philic segment/anchor group of the stabiliser. RAFT/MADIX polymerisation was also adopted for the synthesis of the stabiliser materials within this chapter, because of these reasons.

The synthesis of a range of stabilisers incorporating the monomer VPi, and the subsequent solubility measurements involving these materials, is detailed herein.[48]

3.3.1.1 Synthesis of Homopolymer Stabilisers

Poly(vinyl pivalate) (PVPi) stabilisers of varying targeted molecular weight were synthesised as described using the xanthate RAFT agent (Table 3.1).

Table 3.1: Poly(vinyl pivalate) Homopolymers of Varying Molecular Weight.

Entry	M:R:I	$M_{n,th}$ (kg/mol)	$M_{n,expt}$ (kg/mol)[a]	PDI[a]	D_p[b]	Conv. (%)[c]	T_g (°C)[d]
1	38:1:0.1	4.0	5.0	1.35	37	80	58.9
2	60:1:0.1	6.7	7.8	1.39	59	85	63.3
3	77:1:0.1	8.5	10.0	1.33	76	85	66.7
4	109:1:0.1	11.3	14.3	1.41	110	79	69.7
5	139:1:0.1	15.1	17.5	1.46	135	83	71.3
6	160:1:0.1	18.7	20.5	1.49	159	90	73.9

Polymerisation conditions: Bulk polymerisation at 65 °C for 24 hours with AIBN initiator. [a]Experimental M_n and PDI obtained from GPC-RI detector using PS standards. [b]Degree of polymerisation (D_p) determined using equation 3.1. [c]Conversion determined from ^1H NMR in $CDCl_3$. [d]Glass transition temperature (T_g) values obtained using DSC analysis.

All xanthate terminated homopolymers were purified after polymerisation and were obtained as a white, powder product. The polymer product was dried under vacuum to remove all residual solvent/monomer, as trace solvent impurities can have a significant impact on the solubility in $scCO_2$. If residual monomer/solvent is present it can potentially act as a co-solvent, and improve solubility in CO_2. This will result in a decreased cloud point pressure and compromise the accuracy of the phase behaviour measurements.[49]

The degree of polymerisation (D_p) is defined as the average number of structural units per polymer chain and is calculated using equation 3.2, taking into account the RAFT agent end group that will be incorporated into the final structure.[50] The D_p for the PVPi-X homopolymers shows the way in which the average length of the polymer chain varies, ranging from ~37 monomer units to 159 units.

$$D_p = \frac{M_w\ Polymer - M_w\ RAFT\ agent}{M_w\ Monomer\ Unit}$$

Equation 3.2: Degree of polymerisation calculation, taking the total molecular weight of the polymer and subtracting the molecular weight of the RAFT agent, then dividing by the molecular weight of the monomer/s to give the number of monomer units in a polymer chain.

Monomer conversion was calculated from comparison of monomer and polymer peaks of the ^1H NMR at 4.5-4.6 and 4.8-5.0 ppm respectively (Figure 3.11). Xanthate signals were also detected in the ^1H NMR of the PVPi-X homopolymer, confirming reaction with the xanthate and growth of the polymer chain, with the two components of the RAFT/MADIX agent capping the homopolymer. A broadening of the xanthate signals was observed, characteristic of radical polymerisation procedures.

All signals remained at a similar chemical shift to the xanthate signals prior to polymerisation, with an exception in the case of the methylene group proton in the

xanthate leaving group, denoted as group **c**, which shifted from 4.39 ppm (Figure 3.9) to 2.37 ppm (Figure 3.14). After polymerisation this methylene group proton experiences a change in chemical environment. The proton is no longer in close proximity to the electronegative sulfur atom of the xanthate, and is no longer deshielded, resulting in the observation of the signal at lower shift.

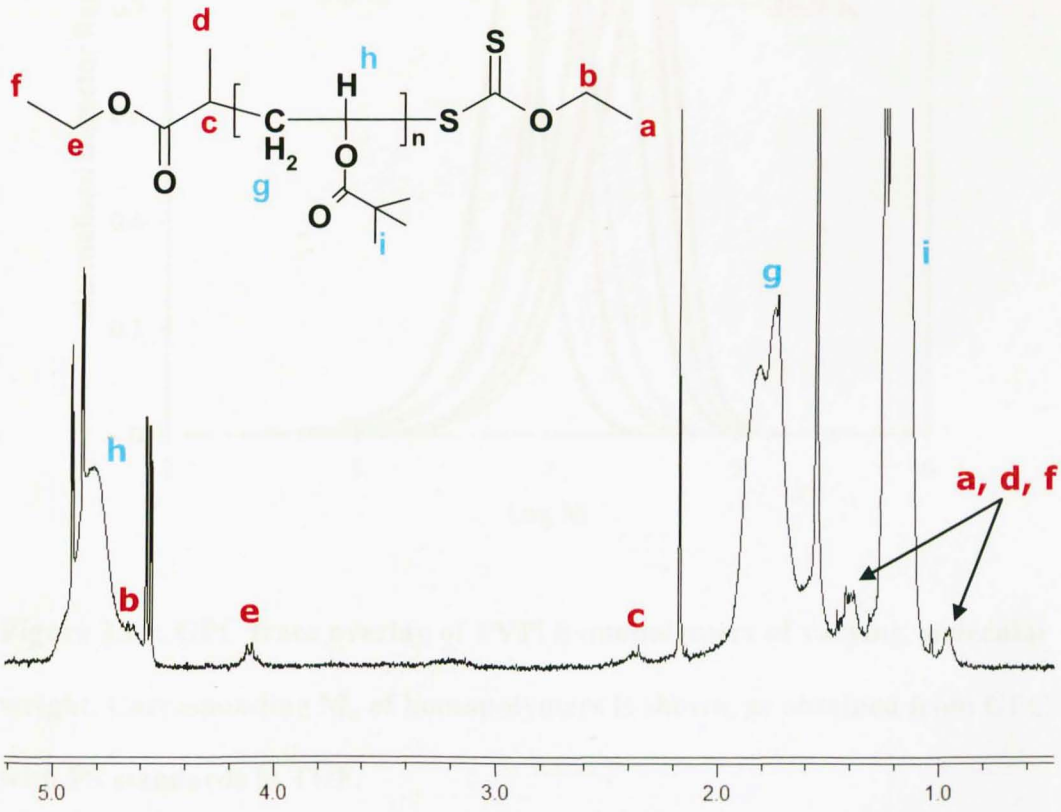

Figure 3.14: Typical ^{1}H NMR of PVPi-X homopolymer in $CDCl_3$. Monomer conversion determined from comparison of integrals of monomer (4.5-4.6 ppm) and polymer (4.8-5.0 ppm) peaks.

Molecular weights achieved were close to $M_{n,th}$, and increasing the proportion of monomer in the reaction led to evolution of the molecular weight to produce longer polymer chains (Figure 3.15).

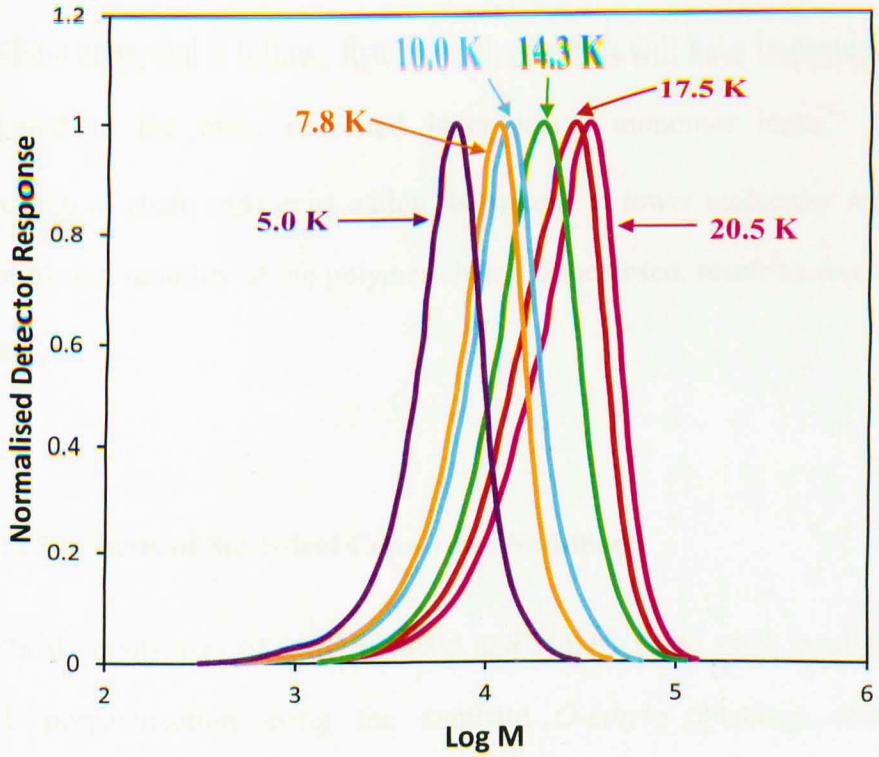

Figure 3.15: GPC trace overlay of PVPi homopolymers of varying molecular weight. Corresponding M_n of homopolymers is shown, as obtained from GPC with PS standards in THF.

PDI values were acceptable (<1.5), indicating a controlled polymerisation, proving xanthate X1 to be effective in the homopolymerisation of PVPi. Overall, PDI appeared to increase with increasing molecular weight, and high conversions were achieved in all polymerisations.

Analysis by DSC also shows T_g values display a slight increase in value as the molecular weight of the sample increased. This is to be expected, as the glass transition temperature has a significant dependence on the molecular weight of linear polymers. Assuming the polymer is linear, each polymer chain will possess two chain ends, and it follows that these chains ends will have improved mobility compared to the more restricted inner repeat monomer units.[51] A higher proportion of chain ends exist within the sample at lower molecular weight, and so the overall mobility of the polymer chains is increased, resulting in a reduction in the T_g value.

3.3.1.2 Synthesis of Statistical Copolymer Stabilisers

Statistical copolymers of vinyl pivalate and vinyl acetate were synthesised *via* RAFT polymerisation using the xanthate *O-ethyl-s-(1-ethoxycarbonyl)ethyl dithiocarbonate*. Copolymerisations were carried out in the same manner as vinyl pivalate homopolymerisations to yield PVAc-*s*-PVPi-X of varying composition and molecular weight (Table 3.2).

The monomer conversion and copolymer composition was determined from ^1H NMR. Composition of the two monomers within the polymer was determined by comparing the relative integrals of the methyl and tertiary butyl groups of VAc and VPi respectively (Figure 3.16). The final copolymer composition varied little from the initial monomer feed ratio, an observation which is attributed in part to the extended reaction time.

Table 3.2: PVAc-*s*-PVPi-X Copolymers of Varying Composition.

Entry	M:R:I	$M_{n,th}$ (kg/mol)[a]	$M_{n,expt}$ (kg/mol)[a]	PDI[a]	Feed Ratio	Expt. Ratio[b]	Conv. (%)[b]
1	143:1:0.1	9.2	8.8	1.60	75:25	72:28	66
2	129:1:0.1	9.1	9.4	1.50	50:50	44:56	65
3	117:1:0.1	8.8	10.3	1.44	25:75	24:76	63
4	117:1:0.1	11.9	10.1	1.59	25:75	24:76	85
5	127:1:0.1	13.6	10.6	1.49	10:90	16:84	85
6	118:1:0.1	12.3	8.9	1.53	8:92	10:90	82
7	117:1:0.1	13.5	9.6	1.45	5:95	6:94	90
8	56:1:0.1	4.5	4.7	1.29	60:40	48:52	74
9	76:1:0.1	5.5	5.7	1.35	60:40	46:54	69
10	151:1:0.1	14.9	13.8	1.50	50:50	48:52	90
11	192:1:0.1	12.4	15.6	1.43	50:50	47:53	62
12	216:1:0.1	16.7	20.6	1.38	60:40	48:52	74
13	260:1:0.1	17.6	21.8	1.47	60:40	48:52	65
14	338:1:0.1	25.9	29.4	1.42	60:40	50:50	74
15	38:1:0.1	3.2	4.5	1.22	15:85	10:90	63
16	60:1:0.1	6.9	7.4	1.42	15:85	10:90	92
17	167:1:0.1	17.4	12.8	1.56	8:92	8:92	83
18	214:1:0.1	15.4	16.5	1.49	8:92	8:92	57

Polymerisation conditions: solution polymerisation in dry toluene (5 mL) at 65 °C for 48 hours, or bulk polymerisation for ~4 hours. Ratios correspond to PVAc:PVPi composition. [a]Experimental M_n and PDI obtained from GPC-RI detector using PS standards. [b]Conversion and PVAc:PVPi ratio determined from ^1H NMR in $CDCl_3$. [c]T_g values obtained using DSC analysis.

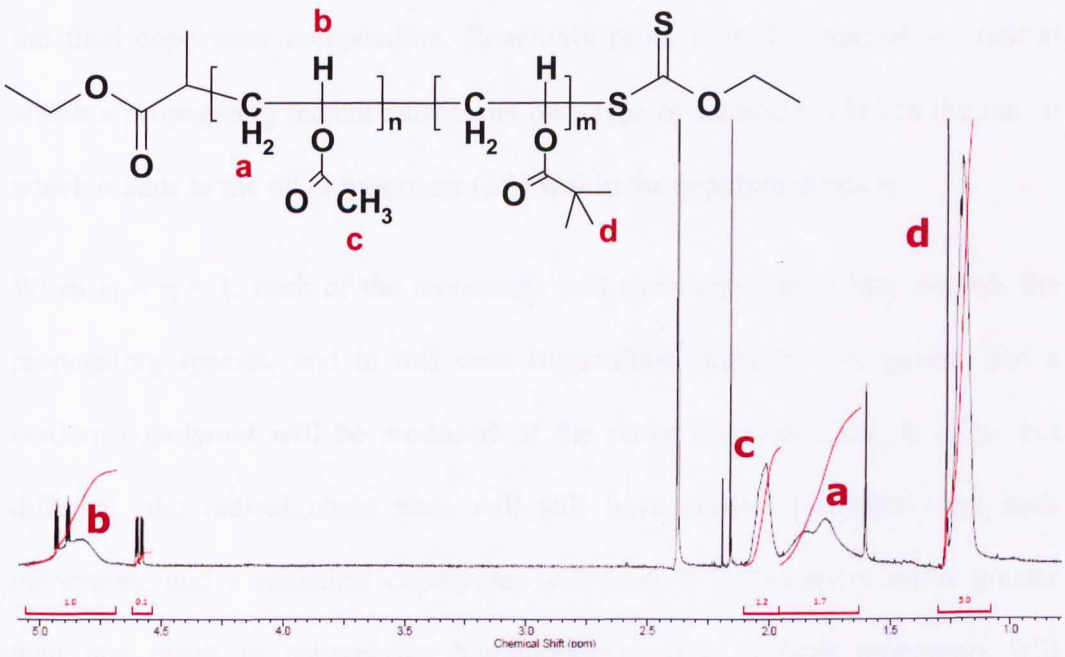

Figure 3.16: ^{1}H NMR of PVAc-*s*-PVPi-X copolymers. Monomer conversion determined from comparison of integrals of monomer (4.5-4.6 ppm) and polymer (4.8-5.0 ppm) peaks.

Molar ratio of PVAc:PVPi is calculated *via* integration of peaks c and d, relating to the CH_3 of PVAc units within the polymer structure, and the ^{t}Bu of PVPi respectively.

For example: Ratio of PVAc : PVPi = (c/3) : (d/9) = 1.2/3 : 5.0/9 = 42 : 58.

When shorter reaction times were employed in a bulk reaction medium, it was necessary to adjust the monomer feed ratio slightly and increase the proportion of VAc to obtain the desired composition. Bulk polymerisations carried out for ~4 h with a 60:40 ratio of VAc and VPi in the monomer feed resulted in a copolymer with ~50:50 final ratio.

The reactivity ratio of the two monomers will have an impact as this determines

the final copolymer composition. Reactivity ratio, r, is the ratio of the rate at which a propagating radical adds to its own type of monomer (M_1) to the rate at which it adds to the other monomer (M_2) within the copolymerisation.

When $r_1 = r_2 = 1$, each of the monomers will show equal reactivity towards the propagating species, and in this case Bernoullian statistics will govern and a random copolymer will be produced. If the ratios are both close to unity, but different, the radical chain ends will still have similar reactivity with both monomers, and a statistical copolymer will form.[52, 53] Reactivity ratios greater than one result in consecutive homopolymerisation as both monomers will preferentially add to monomer M_1.[54] Finally, reactivity ratios close to zero tend to result in alternating copolymer segments.[55]

Reported values for the reactivity ratios of VAc ($r_1 = 0.79$) and VPi ($r_1 = 0.96$) show that the two monomers do not have the same reactivity ratio, but both are close to unity.[56] Therefore the resulting PVAc-*s*-PVPi-X copolymer will have a statistical sequence of monomer units. The presence of the tertiary butyl group enhances the reactivity of the VPi monomer towards radical attack, which is why an increased proportion of VAc is required to obtain the desired ratio.

Copolymers with both a range of molecular weights and ratios were targeted in order to study the effects on CO_2-solubility. Final molecular weights in some cases were higher than that of the theoretical molecular weight at the corresponding conversion, attributed to overestimation via the GPC through the use of PS standards. Overall, target molecular weights could be manipulated

successfully to obtain the desired M_n product (Figure 3.17). All statistical copolymers with varying monomer composition exhibited similar molecular weight distributions, indicating the samples were suitable for comparison of composition.

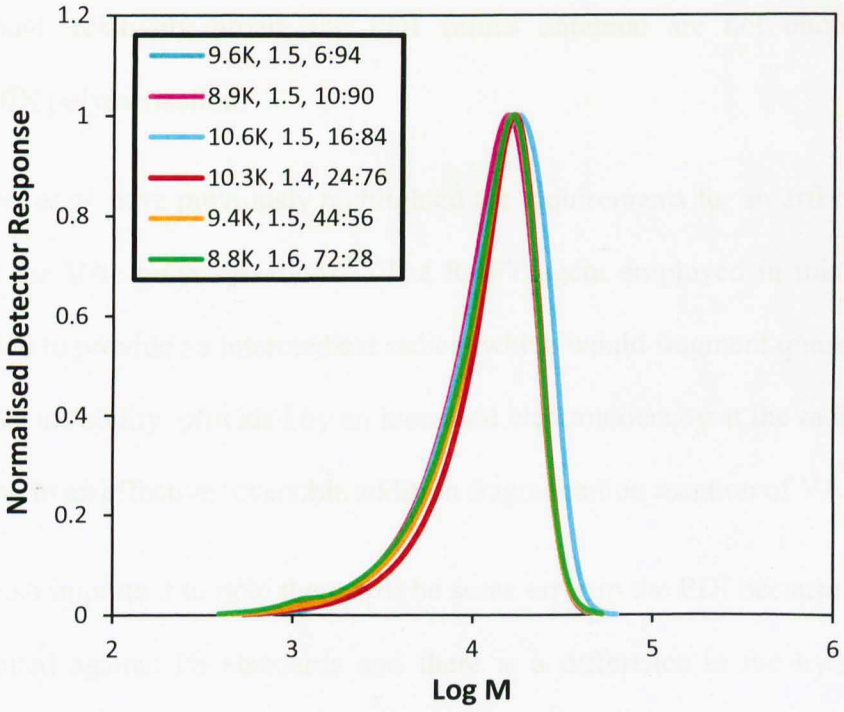

Figure 3.17: GPC trace overlay of PVAc-*s*-PVPi-X copolymers of similar molecular weight and varying PVAc: PVPi ratio. Legend corresponds to: M_n, PDI, PVAc:PVPi ratio. The GPC traces demonstrate the reproducibility of the synthetic procedure and the similarity of the M_n and PDI of the polymers being compared.

VAc is known to be difficult to polymerise; molecular weights are difficult to predict and the PDI of VAc products tends to be high as VAc lacks a conjugating substituent, making its propagating radical less stable and encouraging chain transfer and termination. PDI values were <1.5 in the majority of cases, indicating controlled polymerisation. The broadest PDI (1.56) was exhibited by the copolymer with the largest proportion of VAc moieties in the structure (entry 1). Although relatively broad, the PDI values obtained are not uncommon for MADIX polymerisation.

Stenzel *et al.* have previously highlighted the requirements for an effective RAFT agent for VAc polymerisations.[57] The RAFT agent employed in this work was selected to provide an intermediate radical which would fragment quickly due to a relative instability, provided by an increased electron density at the radical centre, leading to an effective reversible addition fragmentation reaction of VAc.

It is also important to note there will be some error in the PDI because results are calibrated against PS standards and there is a difference in the hydrodynamic volumes of PVPi/PVAc and PS. Absolute molecular weights were also estimated from comparison of the polymer backbone protons and those of the terminal xanthate in the ^{1}H NMR. Molecular weights determined *via* ^{1}H NMR correlated well with the results from GPC analysis (Table 3.3).

Table 3.3 Molecular Weights of Key PVAc-*s*-PVPi-X Copolymer Stabilisers as determined by ^{1}H NMR and GPC-RI.

Polymer	Ratio (PVAc:PVPi)[a]	$M_{n,expt}$ (NMR) (kg/mol)[a]	$M_{n,expt}$ (GPC) (kg/mol)[b]	PDI[b]
PVAc-*s*-PVPi-X	72:28	8.5	8.8	1.6
	44:56	9.0	9.4	1.5
	24:76	10.0	10.3	1.4
	16:84	10.8	10.6	1.5
	10:90	9.6	8.9	1.5
	6:94	10.8	9.6	1.5

[a]Ratio and M_n determined from ^{1}H NMR in $CDCl_3$, with the assumption of one xanthate per polymer chain. Analysis *via* comparison of tertiary butyl group of PVPi (1.18 ppm), methyl group of PVAc (2.00 ppm), and CH_2 group of xanthate (4.11 ppm). [b]Experimental M_n and PDI obtained from GPC-RI detector using PS standards.

Differential scanning calorimetry (DSC) was used to understand the effect of the PVAc:PVPi composition on the thermal properties of the copolymers (Table 3.4).

The glass transition temperature (T_g) was determined by analysis of the large endothermic transition in the second and third heating/cooling cycle. PVAc and PVPi homopolymers are reported to have T_g values of 29 °C and 86 °C respectively.[58] The Fox equation was applied to obtain theoretical glass transition temperatures for comparison with those obtained experimentally.[59]

$$\frac{1}{T_g} = \frac{w_a}{T_{g,a}} + \frac{w_b}{T_{g,b}}$$

Equation 3.2: Fox equation for determination of the theoretical T_g. T_g = copolymer glass transition temperature, $T_{g,a}$ = homopolymer 'a' glass transition temperature, $T_{g,b}$ = homopolymer 'b' glass transition temperature, w_a = weight fraction of monomer 'a', w_b = weight fraction of monomer 'b'.[59]

Table 3.4: Glass Transition Temperatures of PVAc-*s*-PVPi-X Stabilisers.

Entry	$M_{n,expt}$ (kg/mol)[a]	PDI[a]	Expt. Ratio[b]	$T_{g,thr}$[c]	$T_{g,expt}$[d]
1	8.8	1.60	72:28	35.6	32.0
2	9.4	1.50	44:56	46.1	47.4
3	10.3	1.44	24:76	58.4	52.3
4	10.6	1.49	16:84	65.4	57.8
5	8.9	1.53	10:90	71.9	64.6
6	9.6	1.45	6:94	77.0	65.6
7	4.7	1.29	48:52	44.2	46.4
8	5.7	1.35	46:54	45.2	46.7
9	13.8	1.50	48:52	44.2	53.5
10	15.6	1.43	47:53	44.7	56.3
14	4.5	1.22	10:90	71.9	54.0
15	7.4	1.42	10:90	71.9	60.8
16	12.8	1.56	8:92	74.1	66.9

[a]Experimental M_n and PDI obtained from GPC-RI detector using PS standards. [b]PVAc:PVPi ratio determined from ^1H NMR in $CDCl_3$. [c]Theoretical T_g obtained using Fox equation. [d]T_g values obtained using DSC analysis.

This equation does not take into account adjustments due to molecular weight, and this should be taken in consideration when comparing the results (Table 3.4). An additional equation which can be applied for correlation of the T_g with molecular weight is the Flory-Fox equation.[60]

For example, entries 14 and 15 have the same compostion and theoretical T_g, but possess different molecular weights of 4.5K and 7.4K respectively. As a result, a variation in the experimental T_g is observed. The reasons for this are explained in section 3.3.1.1, and attributed to a decreased overall mobility of the polymer chains at higher molecular weights, leading to increased T_g.

As expected, when analysing the copolymers, those with a larger proportion of VPi had a T_g closer to that of PVPi homopolymer, reflecting the decreased flexibility conferred by VPi (Figure 3.18). Some positive and negative deviation from the theoretical T_g was observed, as the Fox equation does not take into account the intermolecular interactions between the polymer components.

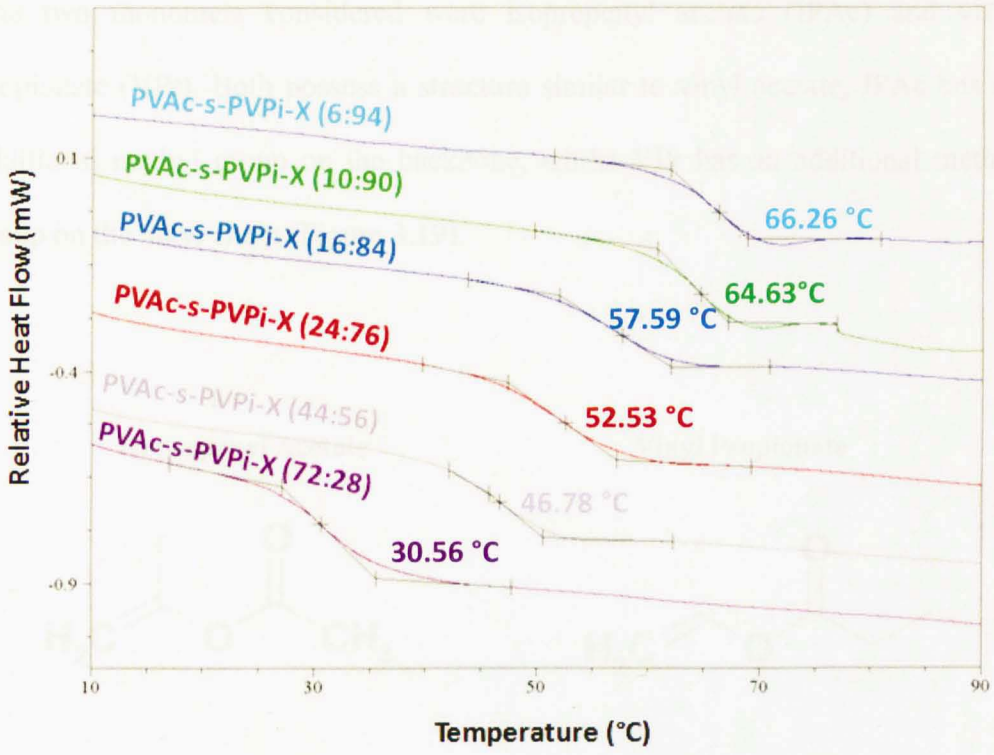

Figure 3.18: DSC curves showing the second cooling cycle for PVAc-*s*-PVPi-X stabilisers of varying composition. Curves exhibit a decrease in T_g value as the proportion of VPi is decreased, owing to the increased flexibility imparted on the material upon incorporation of additional VAc units.

3.3.1.3 Synthesis of VPi-based stabilisers incorporating new monomers

Although the majority of stabilisers synthesised involved VPi and VAc moieties, two other monomers were investigated to determine if using different structures combined with vinyl pivalate had any positive effect on phase behaviour in $scCO_2$.

The two monomers considered were isopropenyl acetate (IPAc) and vinyl propionate (VPr). Both possess a structure similar to vinyl acetate; IPAc has an additional methyl group on the backbone, whilst VPr has an additional methyl group on the alkyl chain (Figure 3.19).

Isopropenyl Acetate **Vinyl Propionate**

Figure 3.19: Structure of the monomers IPAc and VPr.

IPAc was targeted as a potential co-monomer following the reasoning that the addition of a methyl group to the backbone could further increase free volume and improve solubility. VPr was of interest because previous work by Lee *et al.* has proven extension of the alkanoate chain can have favourable effects on solubility, and it was thought the introduction of VPr to the poly(vinyl pivalate) stabilisers might further improve the CO_2-solubility.[35]

The monomer IPAc is difficult to homopolymerise, usually yielding low molecular weight, low melting point polymers. The monomer possesses a large chain transfer constant when compared to monomers such as vinyl acetate and methyl methacrylate. Kuwae *et al.* attribute the problems with

homopolymerisation of this monomer to a high chain transfer to monomer constant (C_m), and the presence of two stable radical conformations, which lead to the two propagating chain ends interchanging at room temperature, resulting in a high rate of chain transfer to the monomer (Figure 3.20).[61]

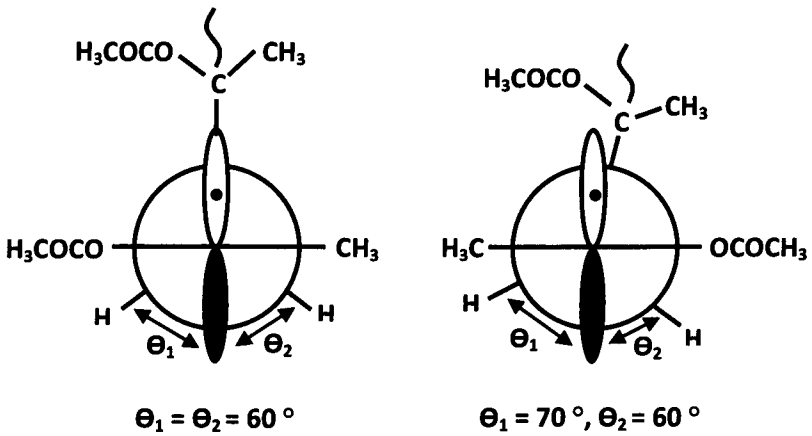

Figure 3.20: Stable radical conformations of propagating radical chain ends of poly(isopropenyl acetate). At room temperature there is an interchange of the β-methylene protons, caused by interconversion of the propagating ends between the two conformations. As a result, the monomer free-radical has little tendency to initiate a new polymer chain.

The high pressure polymerisation of IPAc was recently reported, with some success.[62] The polymerisation was conducted at 10 000 bar (1 GPa) in a high pressure reaction vessel, in which the monomer and initiator were hydrostatically

pressured in silicone oil at 70 °C. It was observed that the use of high pressure favours the linkage of unsaturated monomer into saturated polymer, speeding the polymerisation process and increasing molecular weight significantly, to yield high molecular weight PIPAc. Attempts to homopolymerise IPAc *via* conventional solution polymerisation methods in this study were largely unsuccessful, as expected. Copolymerisation proved slightly more successful, and thus copolymers with ~25:75 feed ratios were targeted for synthesis (Table 3.5).

Table 3.5: Statistical Copolymers of PVPi Incorporating IPAc and VPr.

Copolymer	$M_{n,thr}$ (kg/mol)	$M_{n,expt}$ (kg/mol)[a]	PDI[a]	Ratio[b]	Conv. (%)[b]
PVPr-PVPi-X	10.7	9.9	1.68	25:75	89
PIPAc-PVPi-X	11.2	10.8	1.33	17:83	68
PIPAc-PVPi-X	9.3	8.3	1.45	20:80	62

Polymerisation conditions: Bulk polymerisation at 65 °C for 24 hours, with a feed ratio of 25:75 IPAc/VPr:VPi. [a] Experimental M_n and PDI obtained from GPC-RI Detector. [b] Conversion and ratio determined from ^1H NMR in $CDCl_3$.

Copolymerisation of the two monomers IPAc and VPr with VPi was successful, and polymer products were obtained. For IPAc copolymerisation, it was difficult to obtain a 25:75 ratio, whilst in the case of VPr the feed ratio and experimental ratio were identical. The PDI difference is also significantly higher, and the PVPr copolymer appears to exhibit less control during polymerisation. Whilst reasons for this are unclear, improved control over the PDI could be obtained by terminating the reaction earlier, before such a high conversion is reached.

3.3.2 Phase Behaviour in $scCO_2$

The solubility of the poly(vinyl alkanoate) stabilisers was measured using a hydraulic variable volume view cell, to obtain cloud point measurements and a pressure-temperature phase diagram for each of the stabiliser materials.

The results of a series of studies on polymer solubility in $scCO_2$ are presented and discussed in this chapter. A full description of the variable volume view cell is available in Chapter 2.

3.3.2.1 Homopolymer Molecular Weight in $scCO_2$ + 15 wt% NVP

A series of phase behaviour studies were carried out over a range of molecular weights to determine the solubility properties of the PVPi materials described in Table 3.1. Phase behaviour measurements were determined in $scCO_2$ with 15 wt % NVP monomer with respect to CO_2. The monomer is present to mimic initial dispersion polymerisation reaction conditions.

All cloud point pressures in this thesis were taken three times and an average of these measurements was used, precise to ±0.5-1.0 bar. Temperature of the system was precise to ±0.3 °C.

The monomer acts as a co-solvent, promoting solubility of the hydrocarbon surfactants and enabling phase behaviour to be studied. Without the presence of NVP, the cloud point pressures are much higher and could not all be measured within the pressure constraints of the view cell. The homopolymers behaved as expected with an increase in molecular weight and subsequent chain length

leading to a corresponding decrease in solubility and a higher cloud point pressure (Figure 3.21).

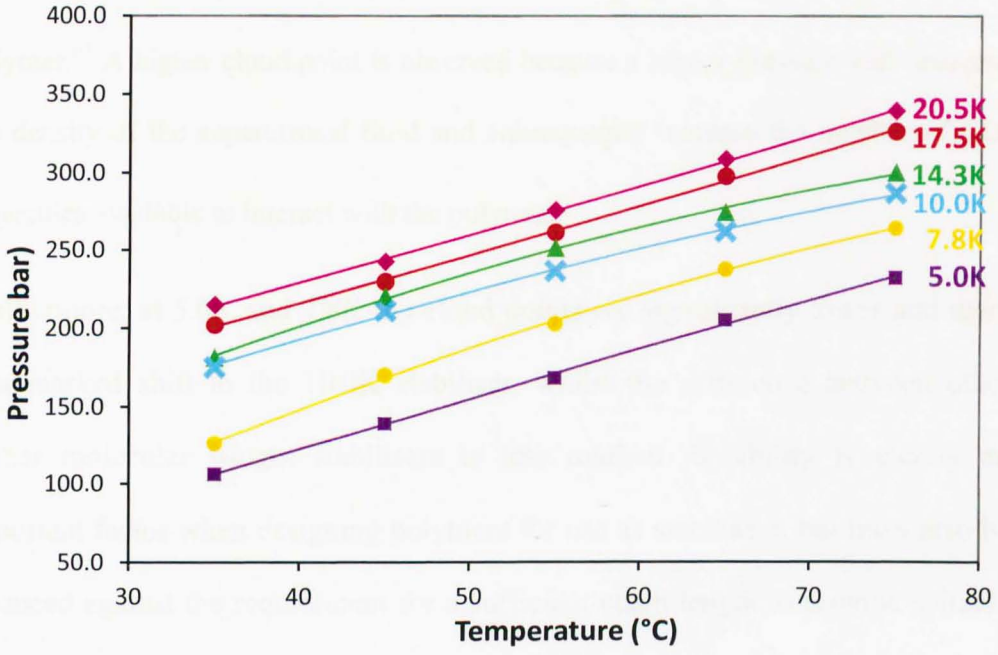

Figure 3.21: Cloud point curves of PVPi-X homopolymers in CO_2 (Table 3.1, entries 1-6). Measurements taken with 15 wt % NVP w.r.t CO_2 and 5 wt % homopolymer w.r.t monomer and clearly show the increase of cloud point pressure with molecular weight. Cloud point pressures were measured three times and an average was used, precise to ±0.5-1.0 bar. Temperature of the system was precise to ±0.3 °C. Error bars are not indicated on the phase behaviour curves as the error is too small to be distinguishable.

These results are in line with observations by O'Neill and coworkers, who compared hydroxy-terminated poly(propylene oxide) of different molecular masses and found the cloud point increased with increasing molecular mass.[5] The effect of

molecular weight can be related to the entropy of mixing. The lower mobility of the the higher molecular weight chains will lead to a reduction in the number of spatial arrangements, restricting the opportunities for CO_2 molecules to interact with the polymer.[63] A higher cloud point is observed because a higher pressure will increase the density of the supercritical fluid and subsequently increase the number of CO_2 molecules available to interact with the polymer.

Furthermore, at 5.0K and 7.8K the cloud points are significantly lower and there is a marked shift to the 10.0K stabiliser, whilst the difference between other higher molecular weight stabilisers is less marked. Solubility is clearly an important factor when designing polymers for use as stabilisers, but must also be balanced against the requirement for a sufficient chain length to provide suitable steric stabilisation in dispersion polymerisations.

3.3.2.2 Copolymer Solubility in $scCO_2$ + 15 wt % NVP

Phase behaviour of the statistical copolymers was carried out to compare the effect of varying composition whilst maintaining a molecular weight of ~10 kg/mol to provide a suitable balance between solubility and stabilising ability (Table 3.6).

The hydrocarbon copolymers were found to possess enhanced solubility with respect to both PVAc and PVPi homopolymers. As might be expected, increasing the proportion of PVPi in the copolymer resulted in a lowering of the cloud point values, and an increased solubility (Figure 3.22).

Table 3.6: Key PVPi-based Stabilisers.

Polymer	$M_{n,expt}$ (kg/mol)[a]	PDI[a]	Ratio (PVAc:PVPi)[b]	D_p[c]	Cloud Point (bar)[d]	T_g (°C)[e]
PVAc-X	9.6	1.39	---	109	229	22.9
PVPi-X	10.0	1.33	---	76	174.8	66.7
	14.3	1.41	---	110	181.0	69.7
PVAc-*s*-PVPi-X	8.8	1.60	72:28	88	167.0	32.0
	9.4	1.50	44:56	84	154.2	47.4
	10.3	1.44	24:76	75	144.8	52.3
	10.6	1.49	16:84	85	136.4	57.8
	8.9	1.53	10:90	70	133.9	64.6
	9.6	1.45	6:94	75	142.1	65.6

[a]Experimental M_n and PDI obtained from GPC-RI detector using PS standards. [b]Ratio determined from ^1H NMR in $CDCl_3$. [c]Degree of polymerisation calculated using M_n and ratio. [d]Cloud point at 35 °C determined using variable volume view cell (100 bar = 1450 psi). [e]T_g values determined from DSC analysis.

Surprisingly, a small proportion of PVAc within the polymer significantly enhances the solubility compared to that of the PVPi homopolymer alone. Whilst VPi units improve solubility through a larger free volume and decreased polymer-polymer interactions, it is also clear that a small proportion of VAc within the structure introduces a certain degree of flexibility to the otherwise rigid polymer. This flexibility is postulated to further improve solubility by enabling the polymers to interact more freely with CO_2, enhancing the entropy of mixing in the solvent. Both residues also possess acetate groups favourable for interaction with CO_2. Somewhat counter-intuitively this means that the PVPi copolymers with a higher T_g actually have greater solubility in $scCO_2$ than those with a low T_g.

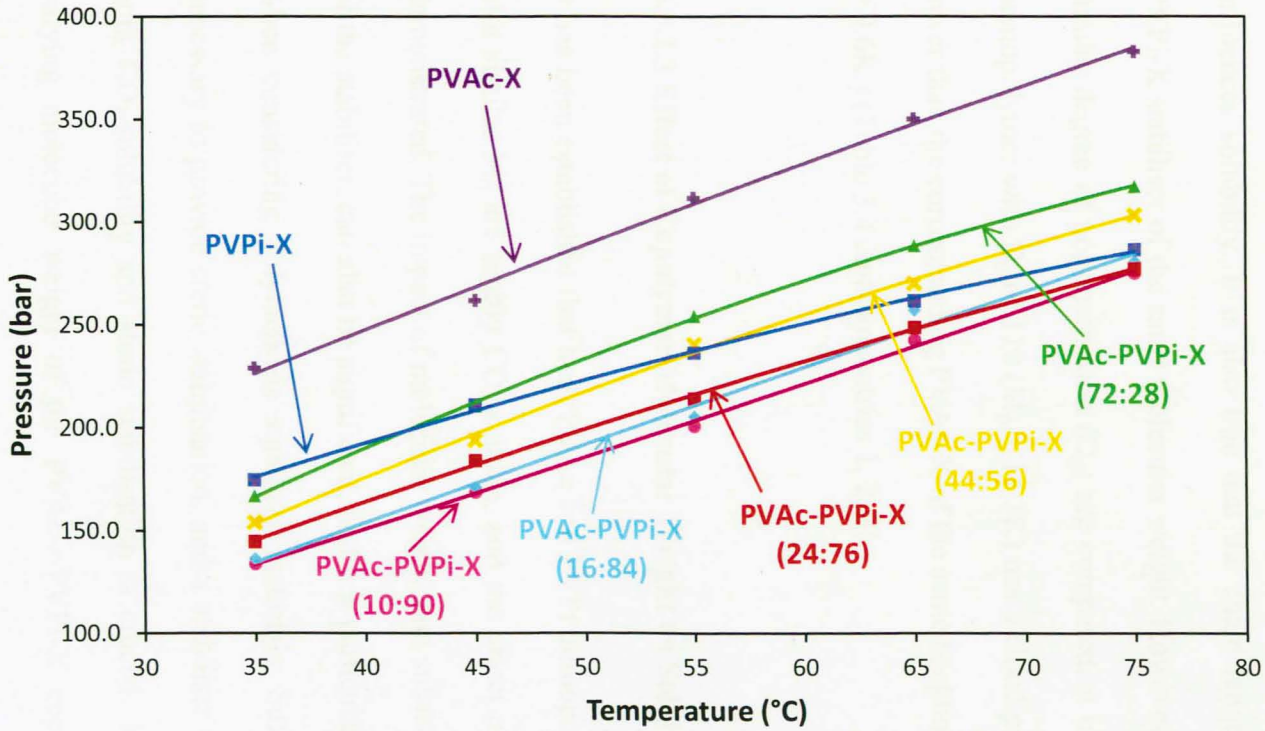

Figure 3.22: Cloud point curves of PVAc-*s*-PVPi-X copolymers M_n~10K in CO_2, with 15 wt % NVP w.r.t CO_2 and 5 wt % homopolymer w.r.t monomer. The data clearly indicate addition of VPi enhances solubility, as the phase behaviour curve is shifted to increasingly lower pressures.

PVPi was also found to be significantly more soluble than the corresponding PVAc homopolymer of the same molecular weight (Figure 3.22). The difference of ~55 bar indicates that the tertiary butyl group of the VPi moiety strongly influences solubility. It is also true that the chain lengths will be shorter in a PVPi-X stabiliser of the same molecular weight. However, if homopolymers with similar degree of polymerisation (D_p) are compared, it is observed that PVPi-X homopolymer with D_p of 110 (M_n = 14.3K) has a cloud point that is still ~ 49 bar lower than the corresponding PVAc-X of the same backbone length (D_p = 110, M_n = 9.6K) (Table 3.4 compare entries 1, 2, 3).

3.3.2.3 Effect of Copolymer Molecular Weight on Solubility in $scCO_2$+NVP

It has been established that both PVAc and PVPi homopolymers and copolymers of a similar M_n are highly CO_2-soluble, and the effect of composition has been demonstrated. The impact of molecular weight, and subsequently the chain length of the stabiliser, can also be significant, and is a particularly important parameter when considering polymers as stabiliser materials. Sufficient chain length is necessary to provide steric stabilisation, and a stabiliser which is able to impart both CO_2-solubility and steric stabilisation is crucial. Therefore, the effect of varying molecular weight of the PVAc-*s*-PVPi-X copolymers on the phase behaviour in $scCO_2$ + NVP co-solvent was investigated. (Table 3.7).

Higher and lower molecular weight copolymers with both 50:50 and 10:90 feed ratio were targeted and tested (Table 3.7, entries 1-8 and 9-13 respectively).

Table 3.7 Key Copolymer Stabilisers of Varying Molecular Weight and at Two Distinct Compositions.

Entry	$M_{n,expt}$ (kg/mol)[a]	PDI[a]	Ratio (PVAc:PVPi)[b]	D_p[c]	Cloud Point (bar)[d]
1	4.7	1.29	48:52	43	106.3
2	5.7	1.35	46:54	52	131.9
3	9.4	1.50	44:56	89	154.2
4	13.8	1.50	48:52	131	179.6
5	15.6	1.43	47:53	150	193.2
6	20.6	1.38	48:52	197	206.1
7	21.8	1.47	48:52	208	213.7
8	29.4	1.42	50:50	282	233.4
9	4.5	1.22	10:90	35	101.2
10	7.4	1.42	10:90	58	117.4
11	8.9	1.53	10:90	71	133.9
12	12.8	1.56	8:92	102	169.1
13	16.5	1.49	8:92	130	194.6

[a]Experimental M_n and PDI obtained from GPC-RI detector using PS standards. [b]Ratio determined from ^1H NMR in $CDCl_3$. [c]Degree of polymerisation calculated using M_n and ratio. [d]Cloud point at 35 °C determined using variable volume view cell.

As expected, the molecular weight trend is the same as observed for the PVPi homopolymers. As molecular weight increases, the solubility in $scCO_2$ decreases, reflected by an increase in the cloud point pressure for each of the stabilisers. As the chain length is shortened, dissolution of the stabilisers in $scCO_2$ occurs more easily (Figure 3.23 and 3.24). This highlights the significant effect molecular weight of the stabiliser will exert on phase behaviour in $scCO_2$. The same cloud point trend for molecular weight was observed for both ratios of PVAc:PVPi.

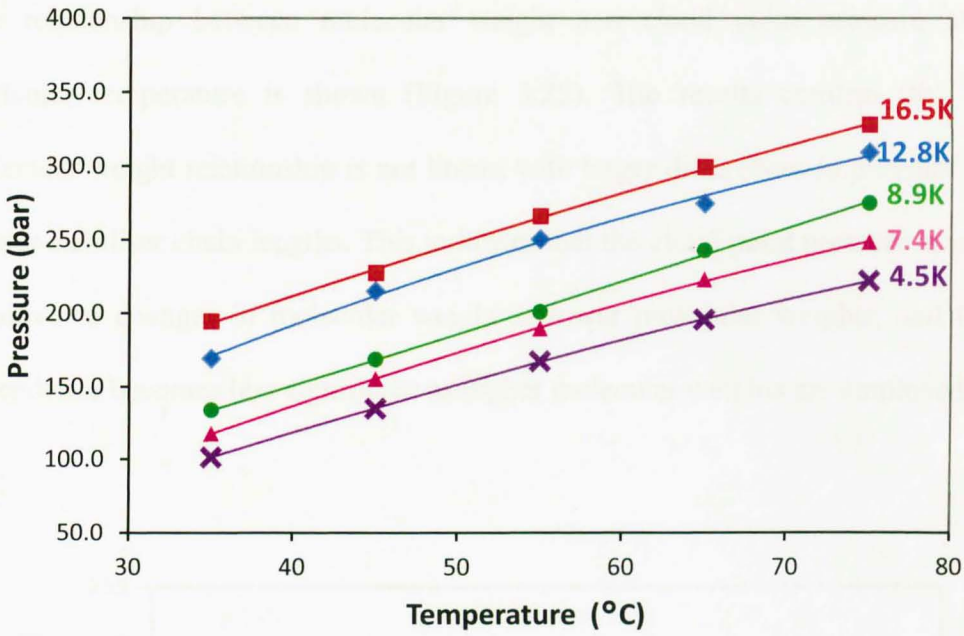

Figure 3.23: Cloud Point curves of copolymers of varying molecular weight with feed ratio of 10:90 and comparable PDI (Table 3.7, entries 1-8).

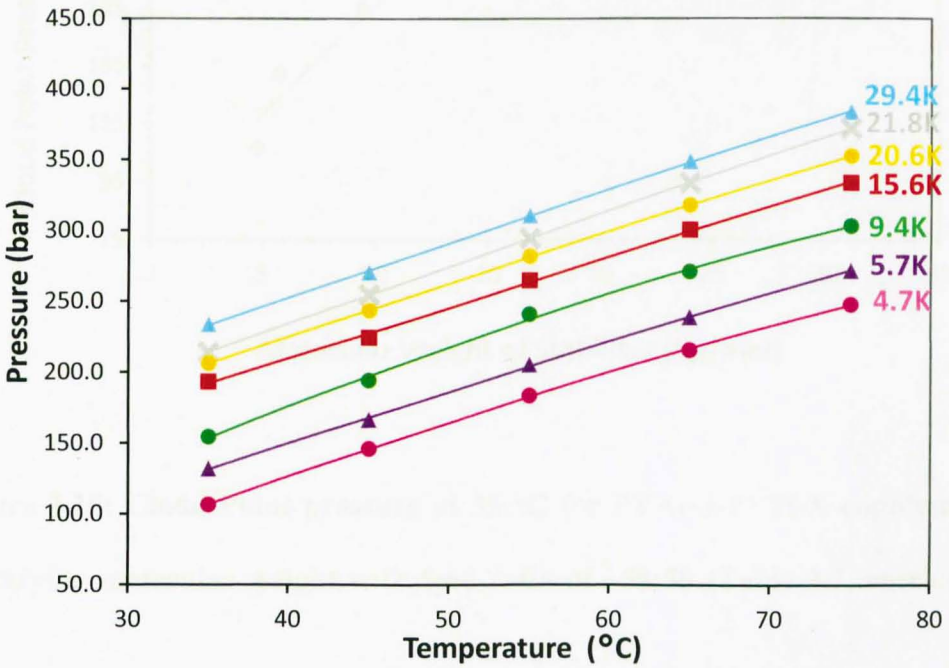

Figure 3.24: Cloud Point curves of copolymers of varying molecular weight with feed ratio of 50:50 and comparable PDI (Table 3.7, entries 9-13).

The relationship between molecular weight and cloud point pressure at a particular temperature is shown (Figure 3.25). The results confirm that the molecular weight relationship is not linear, with larger differences in pressure for shorter stabiliser chain lengths. This indicates that the cloud point pressure is very sensitive to changes in molecular weight at lower molecular weights, and this dependence becomes less significant as higher molecular weights are employed.

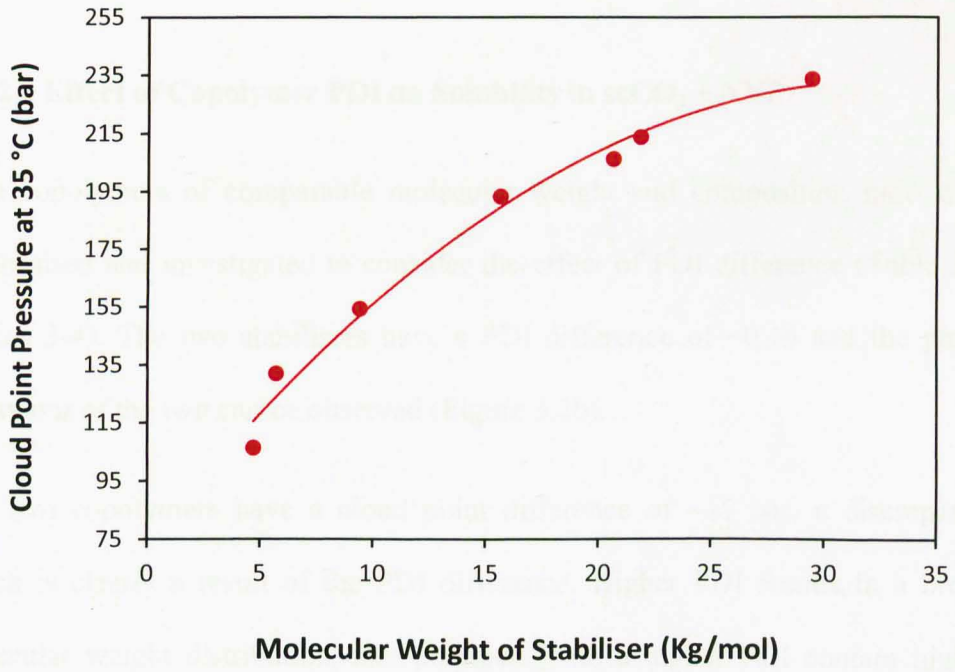

Figure 3.25: Cloud Point pressure at 35 °C for PVAc-*s*-PVPi-X copolymers of varying molecular weight with feed ratio of ~50:50 (Table 3.7, entries 9-13).

Overall, the molecular weight of the stabiliser, and the subsequent D_p of the polymer, is observed to have a distinct impact. A higher D_p will result in decreased solubility. However, a sufficient chain length will be required if the poymer is to act as a suitable material for steric stabilisation in dispersion polymerisation,. Therefore, a balance between these two parameters must be achieved. The effect of the stabiliser chain length in dispersion polymerisations will be discussed in Chapter 4.

3.3.2.4 Effect of Copolymer PDI on Solubility in $scCO_2$ + NVP

Two copolymers of comparable molecular weight and composition ratio were synthesised and investigated to consider the effect of PDI difference (Table 3.2, entries 3-4). The two stabilisers have a PDI difference of ~0.15 and the phase behaviour of the two can be observed (Figure 3.26).

The two copolymers have a cloud point difference of ~15 bar, a discrepancy which is clearly a result of the PDI difference. Higher PDI results in a broad molecular weight distribution, and polymers with a higher PDI contain higher molecular weight chains, which are less soluble in $scCO_2$. These therefore affect the overall dissolution of the polymer chains in CO_2 compared to the low PDI equivalent, thus reducing solubility.

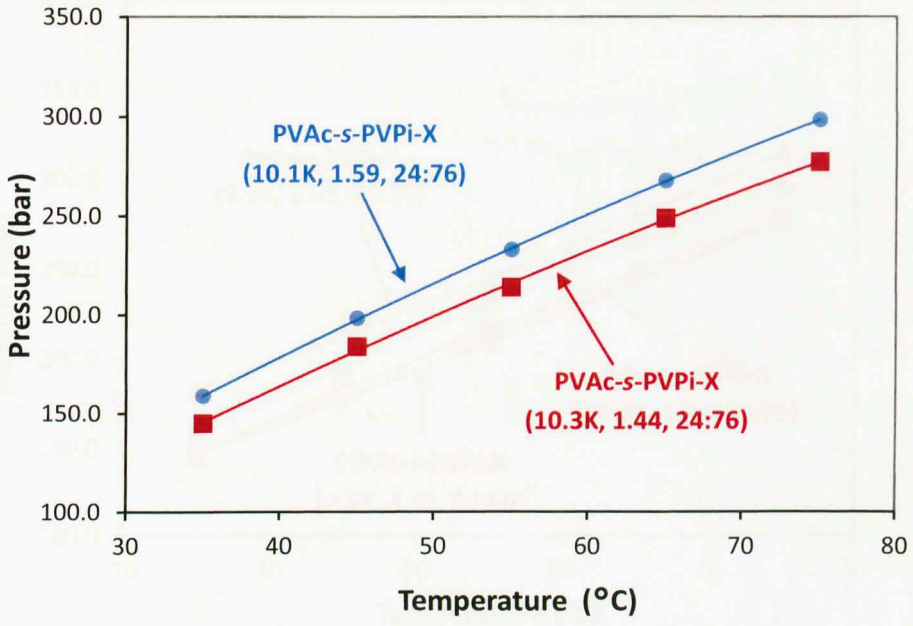

Figure 3.26: Phase behaviour of copolymers with varying PDI and comparable M_n and PDI. Copolymer stabiliser data obtained from Table 3.2, entries 3-4.

In the case of the more polydisperse sample, the higher molecular weight fractions dominate the phase behaviour, and cause the overall cloud point pressure to increase, resulting in decreased solubility of PVAc-*s*-PVPi-X (10.1K, 1.59, 24:76) compared to PVAc-*s*-PVPi-X (10.3K, 1.44, 24:76).

3.3.2.5 Variation of Copolymer Units

Copolymers of VPi were synthesised using co-monomers IPAc and VPr (Table 3.5). The phase behaviour of the resulting copolymers was considered (Figure 3.27).

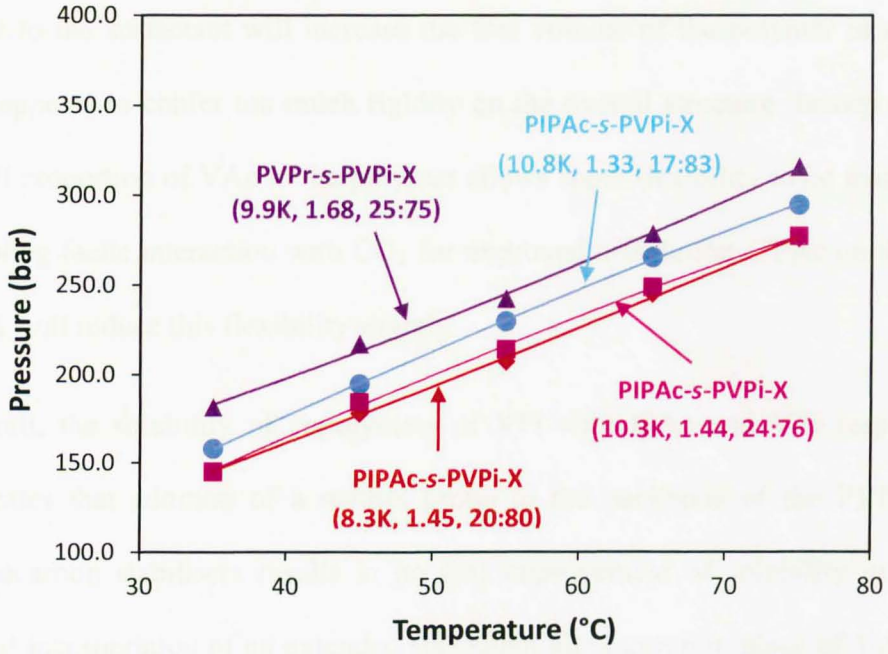

Figure 3.27: Phase Behaviour of copolymers containing VPr and IPAc residues, and comparison with an equivalent PVAc-*s*-PVPi-X copolymer (Table 3.5).

The PVPr-*s*-PVPi-X copolymer has poor solubility compared to the VAc equivalent. The cloud point at 35 °C is 181 bar, compared to 158 bar for PIPAc-*s*-PVPi-X (10.3K, 1.44, 24:76). This may be due in part to the broad PDI of the VPr copolymer when compared to the other copolymers.

PIPAc-*s*-PVPi-X copolymers have solubility approaching that of the VAc/VPi copolymers, with an average cloud point of 158 bar (10.8K) at 35 °C, compared to 145 bar for 10.3K PVAc-*s*-PVPi-X. The methyl group on the backbone appears to reduce solubility to some extent, and this can be attributed to the reduced flexibility the polymer backbone will possess. Whilst addition of both VPi and

IPAc to the surfactant will increase the free volume of the polymer in solution, this appears to confer too much rigidity on the overall structure. Incorporating a small proportion of VAc in the polymer allows some flexibility to be maintained, enabling facile interaction with CO_2 for improved dissolution. IPAc on the other hand, will reduce this flexibility slightly.

Overall, the solubility of copolymers of VPi with IPAc and VPr respectively indicates that addition of a methyl group to the backbone of the PVPi based hydrocarbon stabilisers results in no real improvement of solubility in $scCO_2$, whilst incorporation of an extended side chain alkyl group in place of VAc has a negative effect on CO_2-solubility.

3.3.2.6 Variation of NVP Co-Solvent Concentration

A co-solvent will often improve the solubility of materials in CO_2. Co-solvents act by providing specific interactions to solubilise a compound in CO_2.

Examples of this have been reported by McHugh *et. al*, who described the study of ternary mixtures of poly(butyl acrylate)–CO_2–butyl acrylate (BA) and poly(ethyl hexyl acrylate)–CO_2–ethyl hexyl acrylate (EHA).[64, 65] The addition of BA or EHA to the respective polymer–solvent mixtures was found to decrease the cloud-point pressures by up to 1000 bar, attributed to BA and EHA providing favourable polar interactions with the acrylate groups in the backbone of the polymer. This example highlights the positive impact a co-solvent can have on the

dissolution of a polymer in CO_2. However, depending on the toxicity, addition of a co-solvent can often counteract the benefits of using CO_2.

In the case of the polymerisations that will be discussed in this thesis, the monomer employed in polymerisations will also act as a co-solvent, improving solubility whilst avoiding any toxicity issues that might arise from using additional components, since it will be consumed during the polymerisation. The effect of this co-solvent concentration on the solubility of the stabilisers has been considered (Figure 3.28-3.29).

There is a clear reduction in solubility as the concentration of NVP is reduced. This is as expected, as there is less co-solvent available to enhance the solubility of the hydrocarbon stabilisers. The effect is quite dramatic, as reducing the proportion of NVP from 15 wt% to 2.5 wt% leads to a cloud point curve which has now more than doubled in pressure. A similar overall trend is observed for the copolymer with 10:90 ratio.

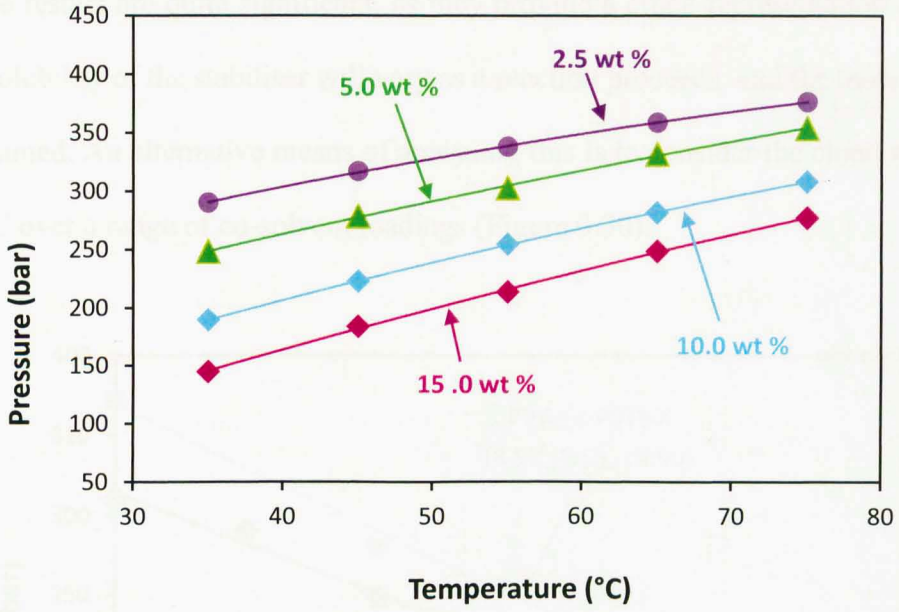

Figure 3.28: PVAc-*s*-PVPi-X (10.3K, 1.44, 24:76) at varying NVP concentration and 5 wt % stabiliser w.r.t CO_2. As the concentration of NVP decreases, the cloud point pressures rises.

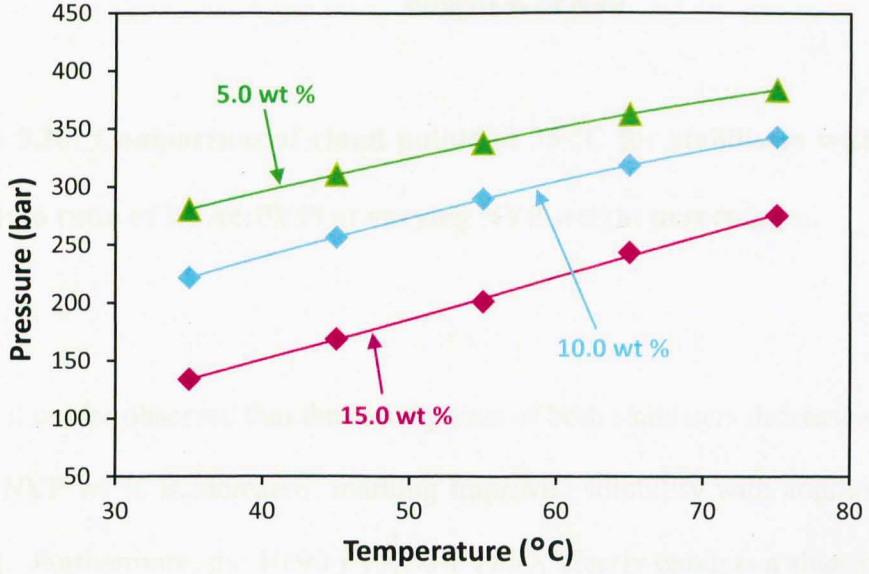

Figure 3.29: PVAc-*s*-PVPi-X (8.9K, 1.53, 10:90) at varying NVP concentration and 5 wt % stabiliser w.r.t CO_2.

These results are quite significant, as they provide a crude representation of how the solubility of the stabiliser will vary as a reaction proceeds, and the monomer is consumed. An alternative means of analysing this is to consider the cloud point at 35 °C over a range of co-solvent loadings (Figure 3.30).

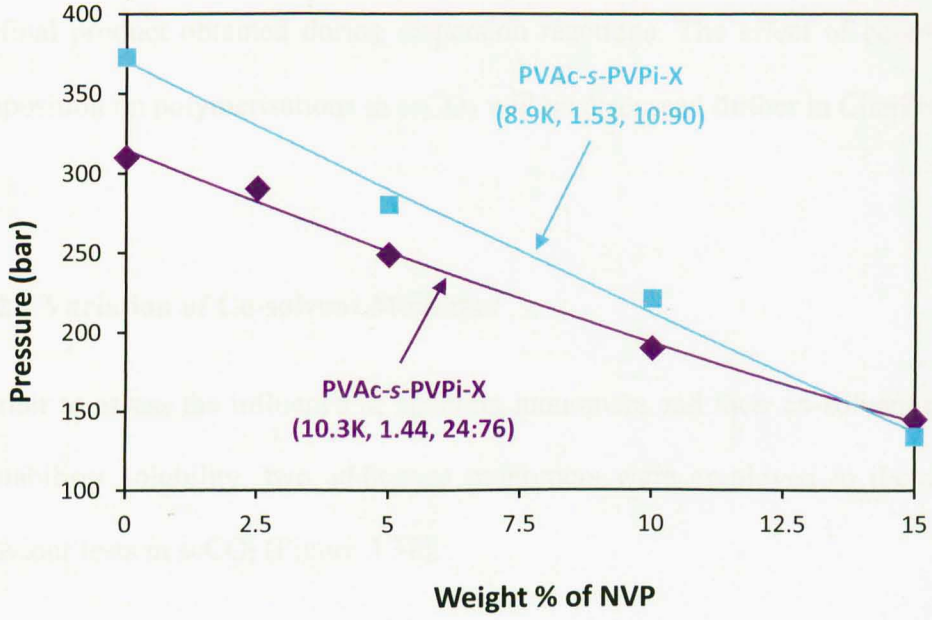

Figure 3.30: Comparison of cloud points at 35 °C for stabilisers with 10:90 and 24:76 ratio of PVAc:PVPi at varying NVP weight percentages.

Again, it can be observed that the cloud points of both stabilisers decrease steadily as the NVP wt % is increased, marking improved solubility with additional co-solvent. Furthermore, the 10:90 PVAc-*s*-PVPi-X clearly exhibits a sharper cloud point curve, and solubility at lower wt % of NVP is much reduced when compared to the 24:76 copolymer equivalent.

These findings could potentially have an effect when the materials are employed as stabilisers. According to the results, as the reaction proceeds and monomer is consumed, PVAc-*s*-PVPi-X (10:90) will become increasingly less soluble in CO_2 compared to PVAc-*s*-PVPi-X (24:76) at corresponding low loadings of NVP. This could have an impact on the ability of the polymer to act as a stabiliser, and the final product obtained during dispersion reactions. The effect of copolymer composition on polymerisations in $scCO_2$ will be discussed further in Chapter 4.

3.3.2.7 Variation of Co-solvent Monomer

In order to assess the influence of different monomers and their co-solvent effect on stabiliser solubility, two additional monomers were employed in the phase behaviour tests in $scCO_2$ (Figure 3.31).

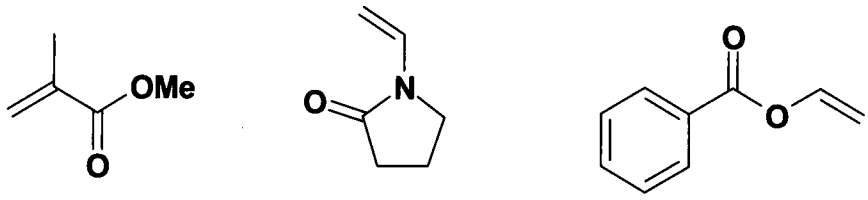

Figure 3.31: Monomers MMA, NVP and VBz, employed as co-solvents in phase behaviour studies in $scCO_2$.

Each monomer varies in structure, and is likely to exhibit differences in solubility in relation to one another. Vinyl benzoate (VBz) contains an aromatic ring, which

will have an impact. Since the aromatic ring of the monomer VBz possesses a quadrupole, this will interact with the quadrupole of CO_2 and increase polarity of the $scCO_2$ reaction medium.[29]

The phase behaviour results using different co-solvents show that there is some impact on overall solubility, and the ring-containing monomers act slightly less effectively, increasing the cloud point pressure to some degree (Figure 3.32).

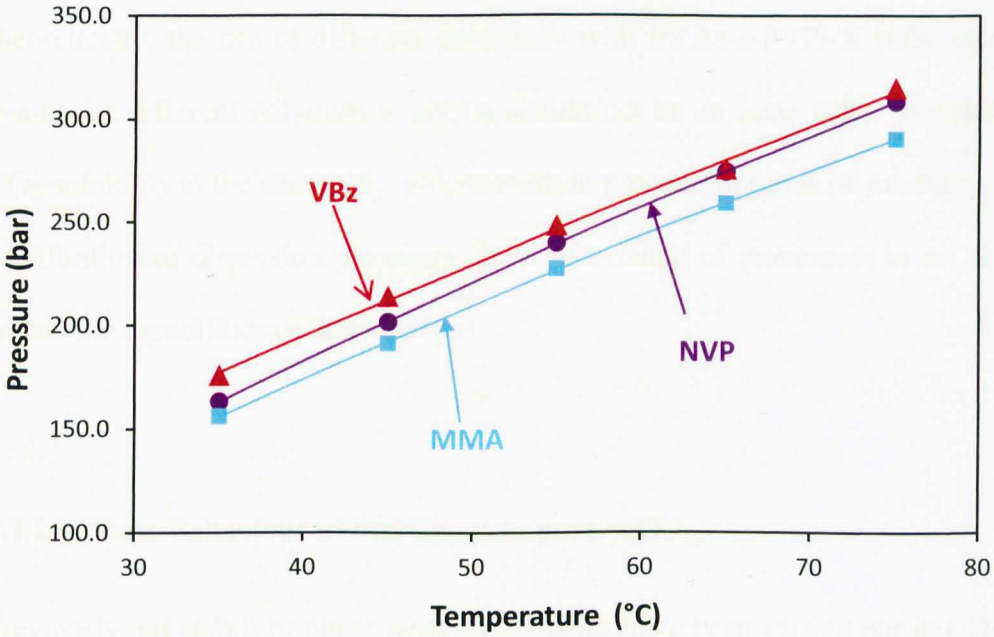

Figure 3.32: Effect of employing monomers NVP, MMA and VBz as co-solvents in phase behaviour studies in $scCO_2$ using PVAc-*s*-PVPi-X (9.0K, 1.43, 54:46).

VBz has the most significant negative impact, which is most likely attributable to the increased polarity, which will make dissolution of the non-polar stabiliser material more difficult. MMA on the other hand, exhibits improved solubility compared to NVP, and appears to interact favourably with the CO_2/polymer system.

However, each monomer is still able to act as a co-solvent and vastly improve the CO_2-solubility of the polymer in question. The variation in solubility between each of the polymer/co-solvent systems is not too drastic. This indicates that theoretically, the use of different monomers with PVAc-*s*-PVPi-X stabilisers to synthesise different polymers in $scCO_2$ should not be an issue when considering CO_2-solubility at the start of the polymerisation process. In terms of solubility, the stabilisation of dispersion polymerisations of a range of monomers in $scCO_2$ is within the capabilities of this stabiliser.

3.3.2.8 Phase Behaviour of Stabilisers in pure $scCO_2$

Previously, all stabiliser phase behaviour studies have been carried out in CO_2 in the presence of the monomer NVP as a co-solvent, to mimic initial high pressure reaction conditions. One reason for carrying out the solubility measurements in these conditions is because hydrocarbon stabilisers have limited solubility in $scCO_2$. As the stabilisers synthesised in this study have significant CO_2-solubility, a selection of the stabilisers were also tested for solubility in pure CO_2. The cloud point curves can be compared (Figure 3.33).

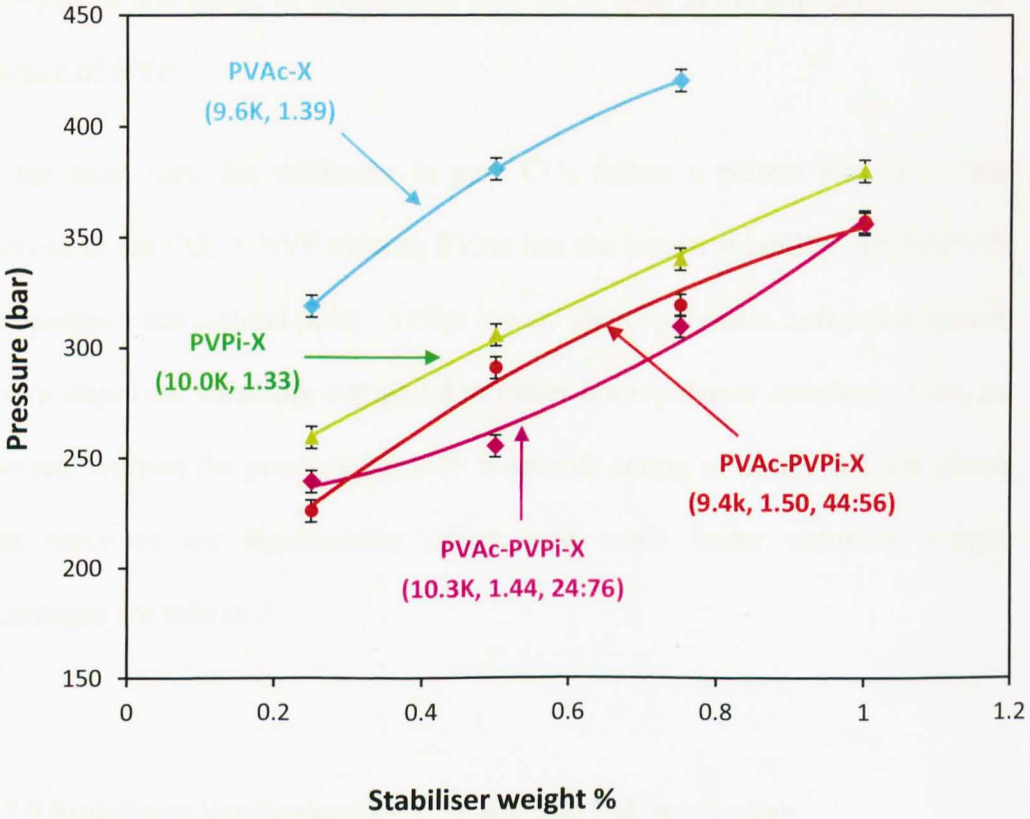

Figure 3.33: Phase behaviour of key stabilisers in pure $scCO_2$ at 35 °C, at varying stabiliser weight percentages. Vertical error bars estimated from experimental results as ± 5 bar.

The phase behaviour in pure CO_2 gave limited information. The cloud points were indistinct and it was difficult to distinguish an accurate pressure owing to the wide pressure window in which the polymer began to precipitate out of CO_2 and become insoluble. The cloud point became more defined as the stabiliser weight percentage was increased, but this also resulted in higher pressures. It is important to note that only very low stabiliser weight percentages of up to 1 wt % were

employed in this study, in comparison to 5 wt % used in the experiments in the presence of NVP.

For the most part, the stabilisers in pure CO_2 follow a pattern similar to that observed in the CO_2 + NVP system; PVAc has the lowest solubility, whilst PVPi homopolymer has a cloud point ~55 bar lower. The copolymers tested also appear to have improved solubility compared to either homopolymer stabiliser. Also, as expected, without the presence of NVP monomer acting as co-solvent, the cloud point pressures are significantly raised, and much lower stabiliser weight percentages are tolerated.

3.3.2.9 Stabilisers Synthesised by Free Radical Polymerisation

RAFT polymerisation has been used extensively within this thesis to produce hydrocarbon polymers with an incorporated RAFT end-group and a narrow molecular weight distribution. In order to confirm the importance of employing RAFT polymerisation to synthesise the hydrocarbon stabilisers, a series of free radical polymerisations were carried out to produce polymers for comparison with the RAFT synthesised equivalents. The results of the synthesis and phase behaviour of a typical free radical copolymer are detailed (Table 3.8, Figure 3.34). A copolymer synthesised by RAFT polymerisation is included for comparison.

Table 3.8: Free Radical Copolymer Synthesis.

Polymer	$M_{n,expt}$ (kg/mol)[a]	PDI[a]	Ratio (PVAc:PVPi)[b]	DP[c]	Cloud Point (bar)[d]
PVAc-*s*-PVPi	10.0	2.05	29:71	86	252.1
PVAc-*s*-PVPi-X	10.3	1.44	24:76	85	144.8

[a]Experimental Mn and PDI obtained from GPC-RI detector using PS standards. [b]Ratio determined from ^1H NMR in $CDCl_3$. [c]Degree of polymerisation calculated using M_n and ratio. [d]Cloud point at 35 °C determined using variable volume view cell.

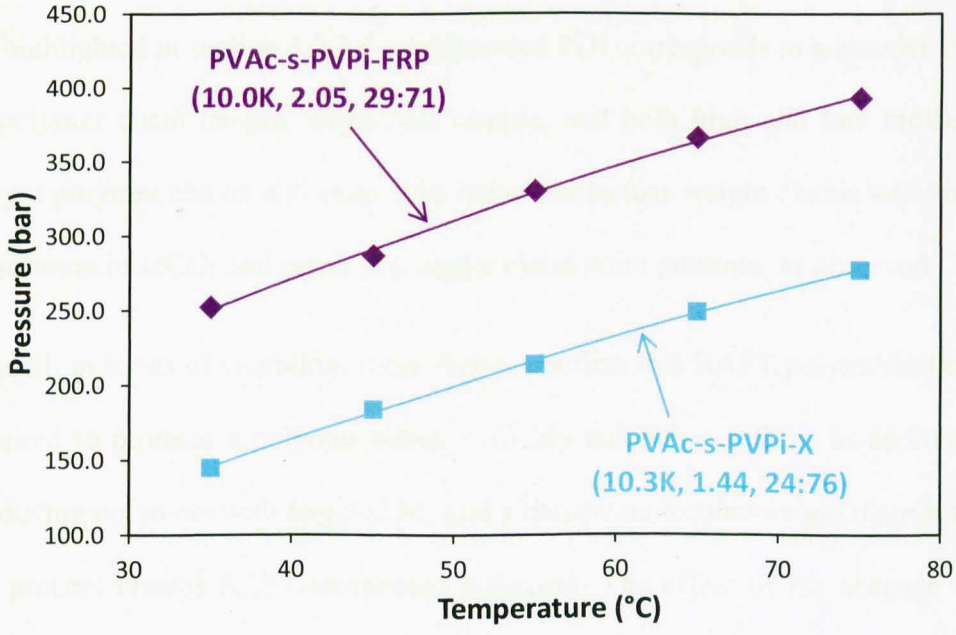

Figure 3.34: Phase behaviour data for PVAc-*s*-PVPi and comparison with xanthate terminated PVAc-*s*-PVPi-X of the same composition and molecular weight.

Phase behaviour data for the stabiliser was determined, and the cloud point values indicated a drastic decrease in polymer solubility for the free radical copolymer (Figure 3.34). The reduction in solubility was much more significant than observed when previously comparing stabilisers of different PDIs that had both been synthesised *via* RAFT polymerisation. The statistical copolymer synthesised by free radical polymerisation has a much broader PDI than that of all RAFT synthesised polymers in this chapter. This is expected, as there is no CTA present during this reaction to control polymer chain growth. Therefore, solubility differences were also anticipated as a result.

As highlighted in section 3.3.2.4, an increased PDI corresponds to a broader range of polymer chain lengths within the sample, and both high and low molecular weight polymer chains will exist. The higher molecular weight chains will hinder dissolution in $scCO_2$ and result in a higher cloud point pressure, as observed.

Overall, in terms of solubility, these results confirm that RAFT polymerisation is required to produce a polymer which is highly soluble in $scCO_2$. In addition to producing polymers with targeted M_n and a narrow molecular weight distribution, the process creates RAFT-terminated polymers. The effect of the absence of a RAFT end-group incorporated in the stabiliser is a key issue in terms of stabilising ability, and will be discussed fully in Chapter 4.

3.4 Conclusions

This chapter has demonstrated that poly (vinyl alkanoate) based stabilisers with high solubility can be successfully synthesised using xanthate mediated RAFT/MADIX polymerisation. Phase behaviour studies have highlighted the significantly improved solubility of both PVPi homopolymers and PVAc-*s*-PVPi-X copolymers as stabilisers. The materials all exhibited a strong dependence between composition and CO_2-solubility. Copolymers comprised of VAc and VPi moieties are significantly more soluble, and increased VPi gives improved solubility. Counter-intuitively, the copolymers with higher T_g are more soluble in $scCO_2$, which can be related to the increased free volume of the stabilisers with a higher proportion of PVPi, and therefore higher T_g.

In addition, the effect of molecular weight, PDI, co-solvent weight percentage and use of monomer alternatives to VAc were assessed. It was established that, as expected, increasing molecular weight significantly affected solubility. PDI had some impact on the polymer solubility; polymers with a broader PDI were solubilised at higher pressure due to the presence of higher molecular weight chains within the distribution compared to the lower PDI equivalent. The monomers VPr and IPAc were found to provide little, if any improvement on the VPi-based copolymer stabilisers. Also, employing different co-solvents had a slight effect on solubility, whilst lowering the percentage of co-solvent employed resulted in a much more dramatic reduction in solubility.

The impact of the RAFT agent attached to the polymer was also considered

through comparison of a polymer synthesised by a typical free radical polymerisation, and a RAFT-synthesised equivalent. It was evident that the RAFT polymerisation technique had a significant effect, and the solubility was vastly improved. This can be easily attributed to the differences in molecular weight distribution leading to decreased solubility in CO_2 as a result of the presence of higher molecular weight chains. The ability to target polymers of specific molecular weight and optimum chain length for improved CO_2-solubility using the RAFT polymerisation technique is a key advantage.

The work presented in this chapter has established that poly (vinyl alkanoate) based stabilisers with high solubility can be successfully synthesised using xanthate mediated RAFT/MADIX polymerisation. Phase behaviour studies have shown the PVAc-*s*-PVPi-X materials are CO_2-philic in nature, and these materials have the potential to be adapted in dispersion polymerisations in CO_2, as an alternative to fluorinated or silicone based surfactants. These solubility studies show great promise and represent a significant step towards inexpensive and effective hydrocarbon stabilisers for application in $scCO_2$.

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Chapter 4: Dispersion Polymerisation Using Hydrocarbon Stabilisers

This chapter builds upon the research in Chapter 3, and details the use of the novel PVPi-based hydrocarbon stabilisers in $scCO_2$.

High pressure polymerisations of *N*-vinyl pyrrolidone using PVPi homopolymer and copolymer stabilisers are compared for their stabilising ability in $scCO_2$. The PNVP products of the high pressure polymerisations are characterised predominantly using SEM to compare particle morphology and ^1H NMR to determine conversion.

4.1 Introduction

4.1.1 Poly (Vinyl Pyrrolidone)

Poly(vinyl pyrrolidone), also referred to as PNVP, is a water soluble polymer synthesised from the monomer *N*-vinyl pyrrolidone (NVP). Reppe was the first to synthesise PNVP, as part of his research into acetylene chemistry, and the first chemical synthesis of this material was patented in 1939.[1]

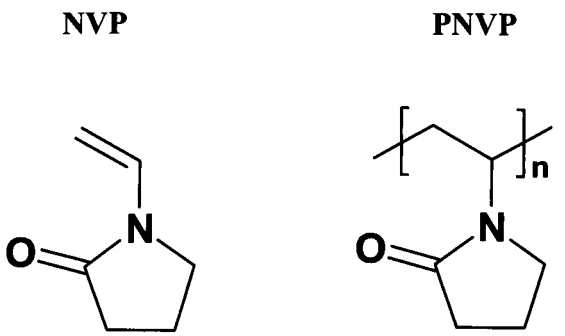


Figure 4.1: The chemical structure of *N*-vinyl pyrrolidone monomer, and the corresponding polymer, poly(vinyl pyrrolidone).

PNVP has remarkable properties. The backbone consists of a carbon chain which possesses a non-polar character, whilst the amide functionality of the pyrrolidone ring repeating unit is highly polar, and capable of forming hydrogen bonds.[2] Because of this, PNVP possesses solubility in water and other polar solvents.[3] As a result of both hydrophilic and hydrophobic functional groups, PNVP has amphiphilic properties which have been exploited in the use of the polymer as a surfactant for heterogeneous systems and their stabilisation.[4] PNVP, in the form

of both a homopolymer and block copolymer, has also been employed in the stabilisation of metal nanoparticles such as gold and silver, coordinating to the metal through the nitrogen and oxygen lone pair electrons of the PNVP chains.[5-9]

Although the monomer is very toxic, the polymer is a stable, biocompatible material which displays good chemical and biological inertness and low toxicity. It has found widespread use in a variety of industries, particularly in pharmaceutical and cosmetic applications, because of these properties.[10] PNVP is marketed for many uses at different molecular weights, ranging from 2,500 g/mol to 1,200,000 g/mol, and the properties vary in accordance with the molecular weights.[11] The polymer is typically assigned a K-value, and this value is related to the weight average of the molecular weight (*e.g.* PNVP K-15 = 6,000-15,000 g/mol) and is obtained from viscosimetric measurements.[3] The glass transition temperature of PNVP will also vary with molecular weight, reaching a plateau of about 175 °C at 100,000 g/mol.[12] At lower molecular weight the T_g will fall to about 100 °C.

PNVP is a hygroscopic substance, and will readily absorb water from the surroundings to appreciably soften.[13] The polymer has found use as a binder and coating aid in pharmaceutical tablets, the hygroscopic character of PNVP being of great importance and playing a role in the binding properties.[10]

The chemical structure of the polymer and the presence of the amide functionality allows PNVP to form a variety of complexes with other chemical compounds including pharmacological actives. One widely used complex is that of PNVP-

Iodine, which is commonly employed as a disinfectant. The solubility of iodine in water is poor, but PNVP will complex iodine and dissolve it in water. The use of PNVP allows a very low level of free iodine to be maintained, leading to effective disinfectants which have very low toxicity.[14, 15]

Copolymerisation of NVP with different monomers can be used to produce polymers of PNVP with varying properties. Copolymerisation with vinyl acetate, which is water-insoluble, reduces the hygroscopicity of the polymer and produces a more hydrophobic material.[16] There are also a range of examples of the synthesis of amphiphilic block copolymers of PNVP, capable of self-assembling into polymeric micelles and representing a promising route for the delivery of drug molecules in biotechnological applications.[17-22]

PNVP can be synthesised *via* bulk, solution or suspension polymerisation. Industrially, the polymer is most commonly synthesised by free radical polymerisation in aqueous solution or in an organic solvent such as 2-propanol, using a peroxide as an initiator.[16] Employing such methods, the polymer is obtained in solution form. As powder products are preferred for pharmaceutical applications, extensive drying processes such as spray drying are often required to isolate the polymer as a solid. Such techniques are often very energy intensive, resulting in them also being rather costly.[11]

4.1.2 Dispersion Polymerisation of PNVP in $scCO_2$

One such technique with the possibly of overcoming the energy intensive drying processes required in conventional PNVP synthesis is the use of $scCO_2$ as a polymerisation medium. Conventional techniques have both economical and ecological disadvantages because of the hazardous organic waste obtained from the reaction in the form of waste solvent, monomer and initiator. As previously mentioned, energy intensive steps are required to dry the polymer at the end of the solution process.

The use of $scCO_2$ as a reaction medium is a highly attractive alternative. It is environmentally benign, non-flammable and also inert towards free radical reactions, making it a suitable medium for polymerisation. The use of $scCO_2$ also allows for simple depressurisation of the reaction mixture upon completion. This allows extraction of all residual monomer and solvents, resulting in the recovery of a pure polymer at the end of the reaction.[23, 24]

PNVP has been successfully synthesised using $scCO_2$ as a reaction medium, *via* dispersion polymerisation employing polymeric surfactants. DeSimone *et al.* first reported the polymerisation of *N*-vinyl pyrrolidone in CO_2.[25] A low molecular weight PFOA stabiliser was employed and the effect of the stabiliser concentration, monomer concentration and CO_2 pressure on the polymerisation was considered.

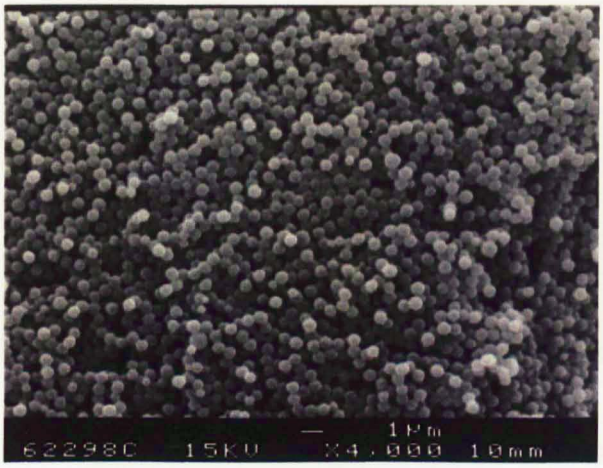


Figure 4.2: PNVP microspheres synthesised using 6 wt % PFOA stabiliser and AIBN initiator at 65 °C and 340 bar.[25]

The use of a PFOA stabiliser yielded micrometer-sized spheres with a relatively narrow size distribution. It was found that increasing the concentration of the stabiliser from 0.5 to 6.0 wt % decreased the particle size diameter, and increasing the monomer concentration increased the particle size. Polymerisations conducted at different pressures were found to have no significant impact on the morphology of the PNVP microparticles.

At the same time, Berger *et al.* also reported the synthesis of PNVP *via* dispersion polymerisation.[26] In this case, the stabiliser employed was a PS-*b*-PDMS diblock copolymer. It was reported that without stabiliser present, a hard, glassy PNVP product was obtained (Figure 5.3, a). In contrast, employing the PS-*b*-PDMS diblock copolymer led to effective stabilisation and the synthesis of uniform, spherical microparticles (Figure 5.3, b).

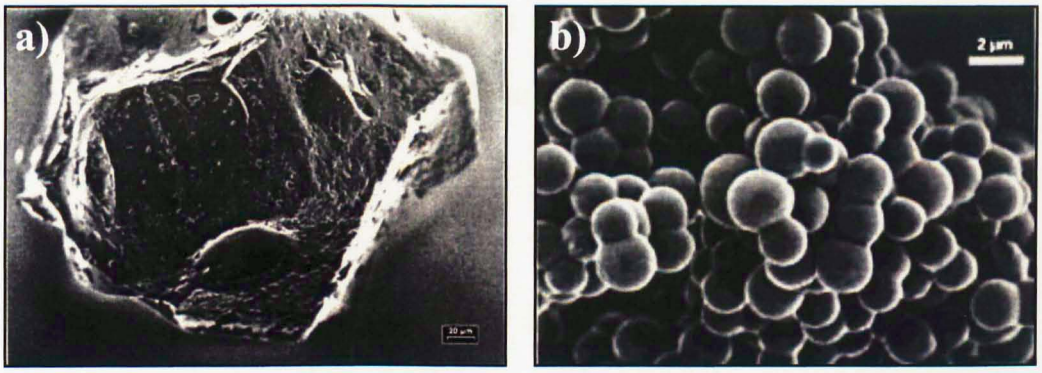


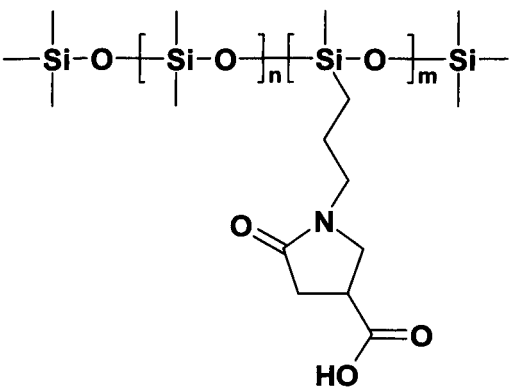
Figure 4.3: SEM micrographs of PNVP particles produced (a) in the absence of stabiliser; (b) in the presence of 1.1 wt % stabiliser.[26]

The reaction parameters were found to have an effect on the PNVP product, and the concentration of the stabiliser had a significant impact. As the stabiliser loading was increased from 0 to 5.1 wt %, a corresponding reduction in particle size was observed as a result of increased surface coverage of the growing polymer particles. A broad molecular weight distribution was also observed, when compared to polymerisation of PNVP under conventional reaction conditions in solution. This was interpreted as a surface plasticisation of the growing particles leading to inhomogeneous polymerisation conditions.[26]

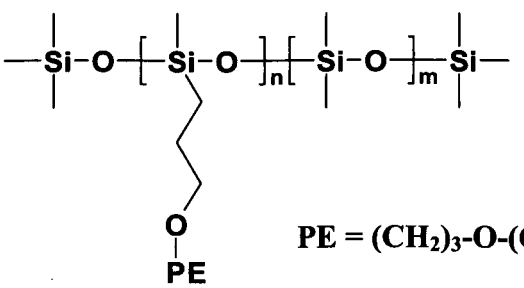
Very recently, Kwon *et al.* reported the preparation of PNVP particles using two stabilisers, siloxane-based polymers Monasil PCA and KF-6017, both of which possess favourable CO_2-solubility and are commercially available.[27] To eliminate flocculation of the resulting PNVP particles and to vary particle size, non-reactive organic co-solvents were added to the polymerisation. The organic solvents were

removed from the PNVP particles with $scCO_2$ extraction. PNVP microparticles were obtained using both Monasil PCA and KF-6017.

a) Monasil PCA



b) KF-6017



$PE = (CH_2)_3\text{-}O\text{-}(C_2H_4O)_x\text{-}(C_3H_6O)_y\text{-}H$

Figure 4.4: Molecular structures of siloxane-based surfactants (a) Monasil PCA; (b) KF-6017.[27]

Particle size of PNVP increased with additional monomer loading (2.0 g to 5.0 g) to the dispersion polymerisation in the case of Monasil PCA, with diameters ranging from 0.41-0.74 μm. No obvious variation was observed with KF-6017 as

a stabiliser and a consistent particle size diameter of 1.02 μm was obtained. The addition of an organic solvent had a particular impact, affecting the solubility of the reaction mixture. Particle size was found to increase significantly (> 2.0 μm) when employing isopropanol as a co-solvent, compared to the dispersion polymerisations in the absence of co-solvent (0.23 μm) and also employing hexane (0.20 μm) and cyclohexane (0.25 μm). The morphology of the PNVP product was also affected, and irregular spheres were observed. In contrast, the particle size diameter was reduced using cyclohexane as a solvent. Finally, the authors used a CO_2 extraction process to remove residual monomer, solvent and surfactant from the PNVP. The silicone level was measured both before and after extraction to determine the presence of siloxane-based stabiliser, and it was observed that the level of silicone after extraction was very low. However, some silicone was still present, indicating that a small proportion of surfactant was strongly adsorbed to the polymer particles and could not be completely removed.

Galia *et al.* also investigated the free radical polymerisation of PNVP in $scCO_2$, using a PDMS-mMA surfactant.[28] The concentration of stabiliser, monomer and initiator were considered, in addition to the density of the fluid phase on the polymerisation. An increase in both stabiliser and AIBN initiator concentration led to a decrease in the particle size of the PNVP product, as did an increase in CO_2 density. The authors concluded that particle size can be controlled by correct selection of the initial surfactant concentration and of the density of the polymerisation system, so that submicron to micron-sized spherical particles can be produced, ranging in diameter from 0.16-5.94 μm. Recently, this research has

been extended to the application of PNVP for controlled drug delivery systems. The synthesis of PNVP was conducted in the presence of two model drugs, ibuprofen and Piroxicam, a drug with low water solubility.[29, 30]

Bae *et al.* determined phase behaviour measurements for the ternary system of PNVP + NVP + CO_2 using a variable volume view cell as a function of molecular weight and NVP content at temperatures up to 450K and pressures up to 2200 bar.[31]

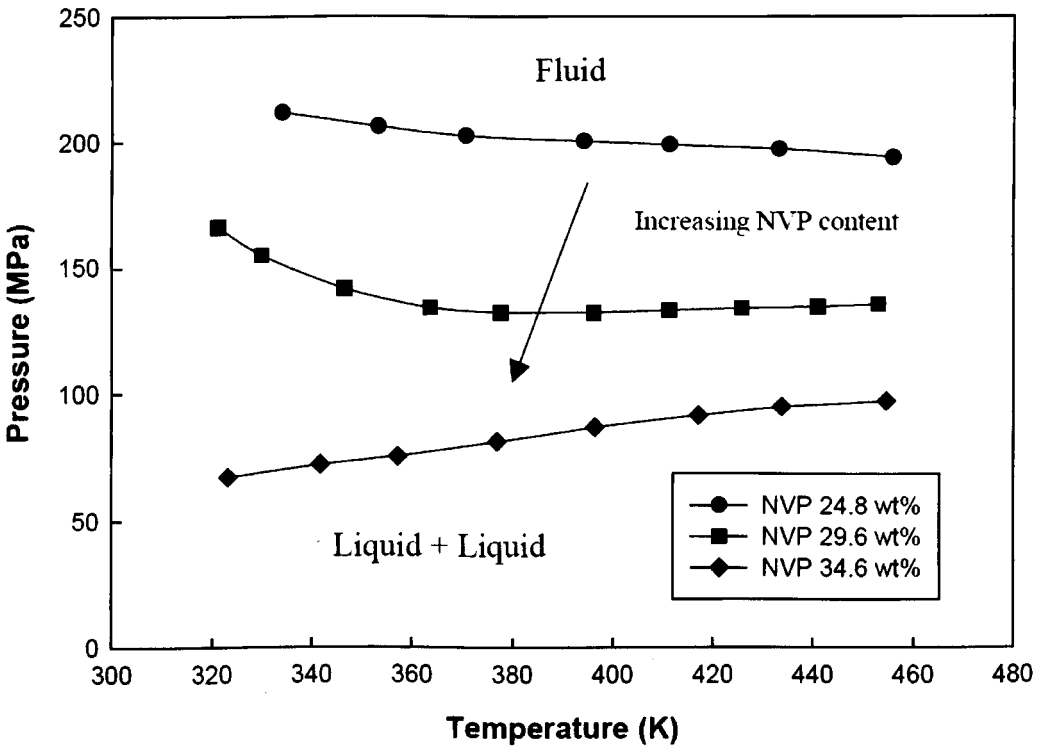


Figure 4.5: Phase behaviour measurements of PNVP (M_w = 2,500 g/mol) + NVP + CO_2 ternary system. As the NVP concentration was increased, the phase behaviour curve shifted to lower pressures, corresponding to an improvement in CO_2-solubility.[31]

It was observed that as the proportion of NVP was increased, the phase behaviour curve was lowered, owing to the increased solubility from the presence of the NVP co-solvent.

In 2010, Kim *et al.* also reported the use of comb-like fluorinated surfactants with different structures for the stabilisation of dispersions of *N*-vinyl pyrrolidone, methyl methacrylate and *N*-vinyl caprolactam in $scCO_2$ (Figure 4.6).[32]

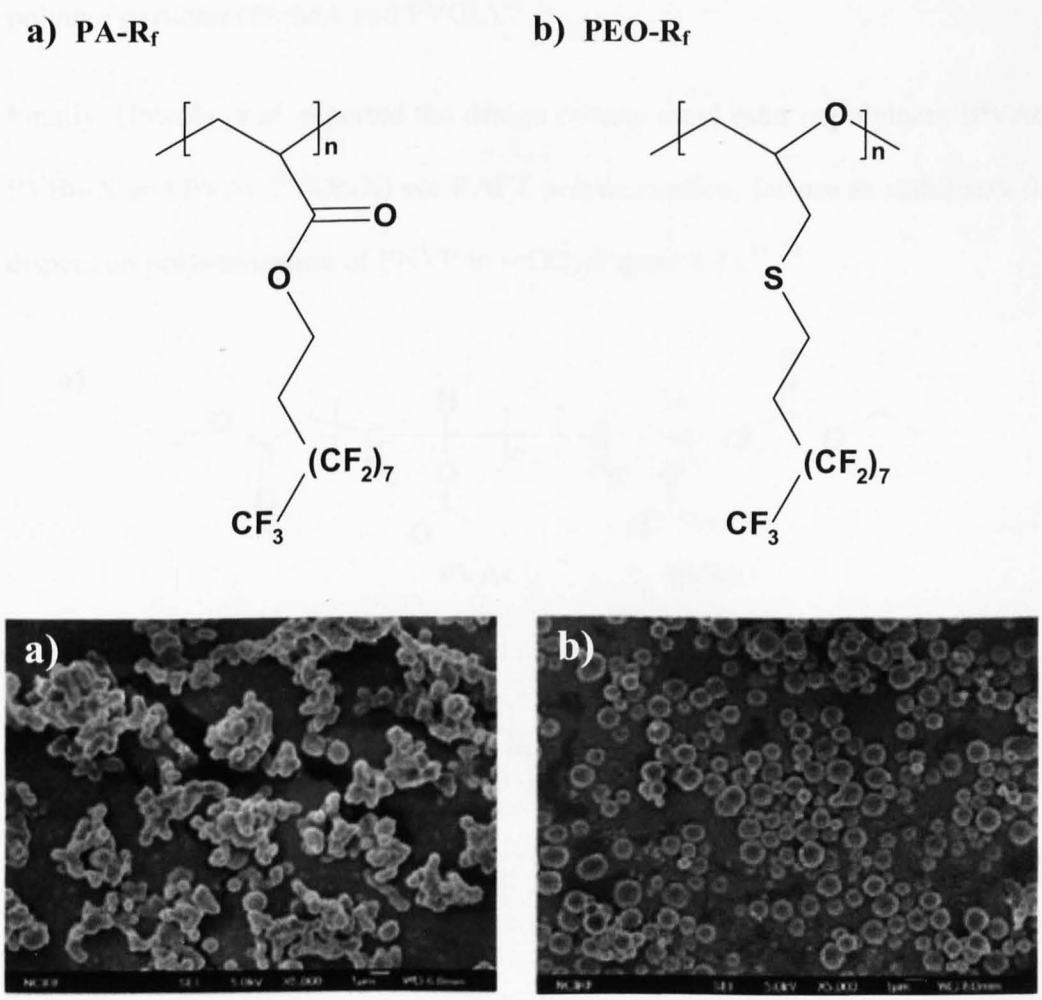


Figure 4.6: SEM images of PNVP products obtained using (a) a stabiliser with non-polar character and (b) a stabiliser with a polar backbone region.[32]

The polarity of the stabiliser was found to determine the dispersion ability; the stabiliser containing a polar oxyethylene in the backbone region (PEO-R_f) acted as an effective surfactant for the polar monomer NVP, producing discrete microparticles, whilst the use of stabilisers with non-polar groups in the backbone region (PA-R_f) resulted in agglomerated structures (Figure 4.6, a-b). It was concluded that PEO-Rf with a more polar backbone can only disperse polar polymer particles (PNVP), whereas PA-Rf can support dispersion of less polar polymer particles (PMMA and PVCL).

Finally, Howdle *et al.* reported the design of new vinyl ester copolymers (PVAc-PVBu-X and PVAc-PVOc-X) *via* RAFT polymerisation, for use as stabilisers for dispersion polymerisation of PNVP in $scCO_2$ (Figure 4.7).[33, 34]

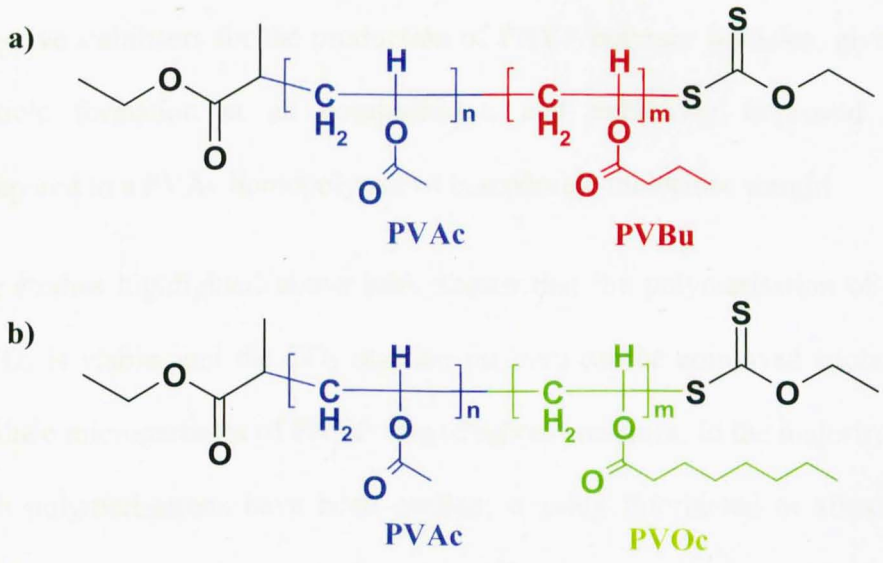


Figure 4.7: Stabilisers of a) PVAc-*s*-PVBu-X and b) PVAc-*s*-PVOc-X used for dispersion polymerisation of NVP in $scCO_2$.[33, 34]

All of the RAFT functionalised vinyl ester copolymers showed an ability to stabilise the growing polymer particles and produce free-flowing powders. Copolymers were determined to possess enhanced CO_2-solubility compared to the corresponding homopolymers of equivalent molecular weight, and thus were able to support dispersion polymerisations in $scCO_2$ more effectively. Depending on the copolymer composition, different particle size, homogeneity and distribution were observed. It was observed that there was a decrease in the size of particles (1.6-1.1 μm) as the proportion of PVBu within PVAc-PVBu-X copolymer stabilisers was increased from 25 to 75 %. The particle size distribution was relatively consistent for all of the stabilisers employed. Conversely, the particle size increased (2.4-4.5 μm) when the PVOc content in PVAc-PVOc-X stabilisers was increased from 25 to 75 %. Overall, the PVAc-PVBu copolymers were effective stabilisers for the production of PNVP polymer particles, giving PNVP particle formation at all compositions, and exhibiting improved solubility compared to a PVAc homopolymer of comparable molecular weight.

The studies highlighted above have shown that the polymerisation of PNVP in $scCO_2$ is viable, and the CO_2 reaction medium can be employed successfully to produce microparticles of PNVP free of solvent residues. In the majority of cases, such polymerisations have been conducted using fluorinated or siloxane-based stabilisers, which are costly and pose an issue to the environment.

Previously in Chapter 3, it was demonstrated that PVPi-based stabilisers possessed enhanced solubility compared to PVAc homopolymers and copolymers of PVAc and PVBu/PVOc. The following chapter investigates the dispersing ability of these CO_2-soluble hydrocarbon stabilisers synthesised in Chapter 3. These polymeric surfactants will be tested in the dispersion polymerisation of PNVP in $scCO_2$, with the aim of identifying viable alternatives to the stabilisers currently employed in such polymerisation reactions.

4.2 Experimental

4.2.1 Materials

N-vinyl pyrrolidone (NVP) (97%, 0.001% *N, N'*-di-*sec*-butyl-p-phenylenediamine inhibitor) was obtained from Fluka. Vinyl acetate (VAc) (99%) and vinyl pivalate (VPi) (99 %) were purchased from Sigma Aldrich. The monomers were stored at 3-4 °C and purified prior to use to remove the inhibitor by passing through a column of activated aluminium oxide, and subsequently degassing *via* three freeze-pump-thaw cycles. The initiator 2,2'-azobis (4-methoxy-2,4-dimethylvaleronitrile) (V-70) (WAKO, 95 %) was used as received. Dry CO_2 (99.99%) and Nitrogen (99.99 %) were purchased from BOC.

4.2.2 Polymer Characterisation

Molecular weight and polydispersity of the PNVP samples were determined using Gel Permeation Chromatography (PL-GPC 50, Polymer Labs) with differential refractometer detection. Chloroform with 5 % triethylamine was employed as the eluent, with two columns (30 cm, PolarGel-M) in series calibrated against PS standards. Yield of the samples was determined gravimetrically. Monomer conversion for all polymers were calculated from the relevant peaks of the ^1H NMR spectra recorded using a Bruker DPX-300 Spectrometer in $CDCl_3$. SEM analysis of PNVP products was carried out using a JEOL 6060L V variable pressure scanning electron microscope. Samples were prepared using a Balzers SCD 030 gold sputter coater. Mean particle diameter (D_n, μm) of the samples was

determined by measuring ~100 particles from SEM data using ImageJ analysis software, and calculating a mean value from these results. The coefficient of variance (C_v) is a statistical measure of the dispersion of the data points in a series around the mean, and was determined using the equation $C_v = (\sigma/D_n) \times 100$, where σ corresponds to the standard deviation of the particle diameter (μm). C_v can be employed to consider the particle size distribution in a typical SEM sample. A sample in which all polymer particles are identical in size would have a C_v of 0.

4.2.3 Synthesis and Polymerisations

4.2.3.1 Polymerisation of NVP in $scCO_2$

The stabilising ability of the polymeric surfactants was determined by employing the materials in dispersion polymerisations in $scCO_2$ to produce poly(vinyl pyrrolidone) (PNVP).

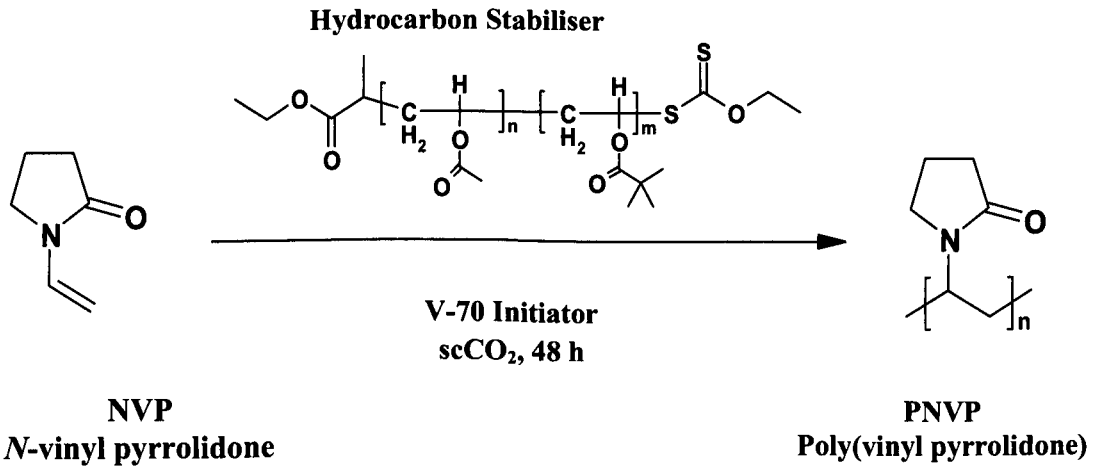


Figure 4.8: Polymerisation of NVP using PVPi-based hydrocarbon stabilisers and V-70 initiator.

A detailed description of the high pressure polymerisation procedure is outlined in Chapter 2, section 2.2.1. The low temperature initiator 2,2′-Azobis-(2,4-dimethyl-4-methoxyvaleronitrile) (V-70) was employed (Figure 4.9). V-70 is an effective

radical initiator at low temperatures compared to AIBN, and has a half life of 10 h at 30 °C.

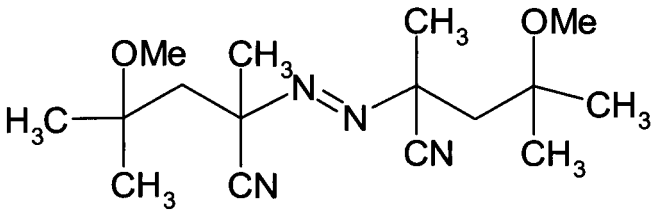


Figure 4.9: The structure of the low temperature initiator V-70.

The initiator was added to a 60 ml Mk III autoclave. Hydrocarbon stabiliser (2.5-15 wt %) was dissolved in NVP monomer (8 ml) and injected through the safety valve into the autoclave. The vessel was filled with CO_2 (~55 bar) and heated to 35 °C, which resulted in an observed increase in pressure to ~ 83 bar. At this point, the cell was topped up to ~276 bar and the reaction proceeded for 48 h with stirring. The autoclave was then cooled to room temperature and the CO_2 vented from the vessel to yield the polymeric product.

4.2.3.2 Hydrocarbon Stabiliser Synthesis in $scCO_2$

In addition to the synthesis of PNVP in high pressure polymerisations in $scCO_2$, attempts were made to produce the hydrocarbon stabilisers themselves in the same reaction medium. The procedure was similar to that of a typical polymerisation in $scCO_2$, but no stabiliser was required as the resulting PVPi

polymer should be soluble in the reaction medium, and the polymerisation was effectively a homogeneous solution polymerisation mechanism. In this case AIBN initiator was employed.

AIBN initiator was added to a 60 ml Mk III autoclave. The VPi monomer (8 ml, 0.06 mol) and xanthate X1 (0.17 g, 7.9×10^{-4} mol) were thoroughly degassed and then injected into the autoclave *via* the safety valve. The vessel was filled with CO_2 (~55 bar) and heated to 65 °C, whilst stirring at 300 rpm. Once at the desired temperature, the cell was topped up to ~276 bar and the reaction proceeded for 48 h with stirring. The autoclave was then cooled to room temperature and the CO_2 vented from the vessel to yield the polymeric product.

4.3 Results and Discussion

4.3.1 Dispersion Polymerisation of NVP

Dispersion polymerisations in $scCO_2$ were carried out using the NVP monomer in order to understand the stabilising ability of the synthesised poly (vinyl alkanoate) materials. Chapter 3 detailed the synthesis of novel hydrocarbon stabilisers which were found to possess favourable CO_2-solubility at various molecular weights and compositions. In addition, the incorporation of a xanthate end-group functionality through the application of RAFT polymerisation provides a potentially effective anchor to the growing PNVP chain which should enable the polymers to act as successful stabilisers.

It is hypothesised that for all RAFT synthesised PVPi-based stabilisers detailed within this thesis that anchoring will occur *via* the RAFT functionality incorporated into the end-group of the polymer (Figure 4.10, a). In this scenario, it is expected that the xanthate functionality acts as a typical RAFT agent, forming a chemical bond with the growing PNVP chains. This will lead to the formation of a block copolymer consisting of the hydrocarbon stabiliser grafted to the PNVP chain, and terminated with the RAFT agent. The xanthate terminated growing PNVP chains will associate and form primary particles. Additional polymerisation will continue within the monomer-swollen particles, leading to high molecular weight PNVP products. As the RAFT agent concentration is very low, no control over the polymerisation is exerted, and the xanthate group will simply provide a means of anchoring to the growing PNVP particle.

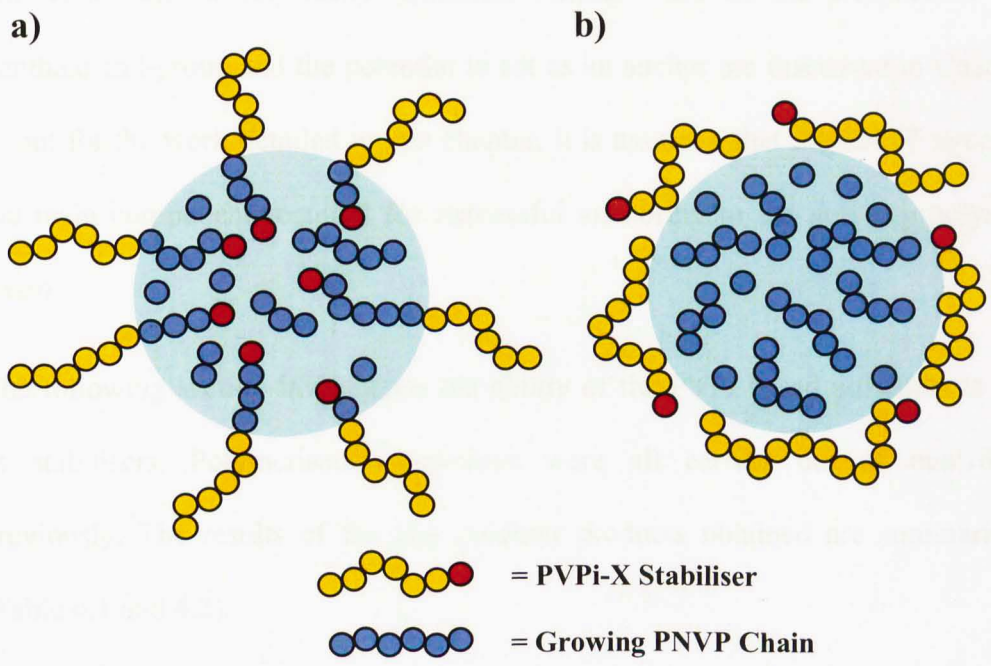


Figure 4.10: Possible modes of anchoring via the PVPi-based stabilisers: a) Chemical anchor mechanism involving RAFT polymerisation of the growing PNVP chains and b) Physical anchor mechanism in which the stabiliser physically adsorbs to the surface of the growing polymer particle.

However, the RAFT exchange mechanism may lead to very low levels of dispersant being loaded at the particle surface. Thus an alternative explanation would be that instead it is anchoring through a physical adsorption mechanism, such as weaker Van der Waals interactions (Figure 4.10, b). This mechanism would involve the formation of primary particles of growing PNVP chains, which are stabilised *via* adsorption of the stabiliser at the surface of the PNVP particle. In this case, the stabiliser would not be chemically bound to the PNVP product

but would still be physically entrained. Further work on the presence of the xanthate end-group and the potential to act as an anchor are discussed in Chapter 5, but for the work detailed in this chapter, it is assumed that the RAFT agent is the main component required for successful anchoring to the growing polymer chain.

The following section investigates the ability of the PVPi-based polymers to act as stabilisers. Polymerisation reactions were all carried out as described previously. The results of the key polymer products obtained are summarised (Table 4.1 and 4.2).

GPC analysis of the PNVP samples obtained from the polymerisations in $scCO_2$ showed molecular weights in the range of 162 to 240 kg/mol. No distinct trends were observed for the molecular weights obtained, and at this loading of stabiliser (5.0 wt %) it was not anticipated that there would be any control of molecular weight of the PNVP by the RAFT functionality. A high initiator loading was used in the majority of cases (stabiliser to intiator ratio of 1:10). An excess of initiator was chosen in order to control the polymerisation at the start, and allow the polymer chains to grow to a sufficiently long length before the RAFT agent incorporated into the stabiliser interferes with the reaction. The RAFT-terminated portion of the stabiliser can then graft to the polymer chains, allowing stabilisation of the dispersion polymerisation. Also, as a consequence of the initiator loading, the concentration of the xanthate group will be too low to exert any control over the radical polymerisation.

Table 4.1: NVP Polymerisations in scCO$_2$.

		Stabiliser		PNVP Dispersion Product					
Entry	**Composition**	**M_n, PDI, Ratio[a]**	**Cloud Point (bar)[b]**	**M_w(kg/mol)[c]**	**PDI[c]**	**D_n (μm)[d]**	**C_V (%)[e]**	**Yield (%)[f]**	**Conv. (%)[g]**
1	PVPi-X	10K, 1.33	174.8	233	4.1	2.2	41.2	94	99
2		14.3K, 1.41	181.0	234	4.7	1.9	26.3	88	>99
3		9.6K, 1.46, 6:94	142.1	240	6.1	2.8	26.9	84	99
4		10.6K, 1.49, 16:84	136.4	236	5.1	2.4	22.6	86	99
5	PVAc-*s*-PVPi-X	10.3K, 1.44, 24:76	144.8	219	4.7	1.7	28.0	90	98
6		9.4K, 1.50, 44:56	154.2	162	4.2	1.4	30.2	86	>99
7		8.8K, 1.60, 72:28	167.0	186	4.4	1.3	31.3	82	99

Polymerisation conditions: scCO$_2$ polymerisation at 35 °C for 48 hours with V-70 initiator and 5 wt % of stabiliser. [a]Stabiliser M_n and PDI determined *via* GPC-RI with THF eluent and PS standards, Ratio determined from ^{1}H NMR. [b]Stabiliser cloud point determined using variable volume view cell. [c]Experimental M_w and PDI obtained from GPC-RI detector in chloroform with 5 % triethylamine using PS standards. [d]Mean particle diameter as determined from sampling of ~100 particles of a typical SEM image. [e]Coefficient of variance as determined by equation $C_v = (\sigma/D_n) \times 100$. [f]Yield determined gravimetrically, recording the weight of the final polymer product. [g]Conversion determined from comparison of monomer and polymer peaks in ^{1}H NMR spectra using $CDCl_3$.

Table 4.2: NVP Polymerisations in $scCO_2$ using PVAc-*s*-PVPi-X Copolymer Stabilisers of Varying Molecular Weight.

Stabiliser			PNVP Product				
Entry	**M_n, PDI, Ratio[a]**	**Cloud Point (bar)[b]**	**D_n (μm)[c]**	**C_V (%)[d]**	**Yield (%)[e]**	**Conv. (%)[f]**	**Appearance**
1	4.7K, 1.29, 48:52	106.3	-	-	58	97	Hard, Tacky Solid
2	5.7K, 1.35, 46:54	131.9	3.1	20.8	74	96	Powder
3	9.4K, 1.50, 44:56	154.2	1.4	30.2	86	>99	Powder
4	13.8K, 1.50, 48:52	179.6	2.5	23.2	91	97	Powder
5	15.6K, 1.43, 47:53	193.2	2.5	31.0	91	>99	Powder
6	20.6K, 1.38, 48:52	206.1	2.6	23.0	93	94	Powder
7	21.8K, 1.47, 48:52	213.7	3.1	24.6	83	>99	Powder
8	29.4K, 1.42, 50:50	233.4	-	-	57	98	Hard, Tacky Solid
9	4.5K, 1.22, 10:90	101.2	-	-	82	89	Powder
10	7.4K, 1.42, 10:90	117.4	3.0	48.7	87	>99	Powder
11	8.9K, 1.53, 10:90	133.9	2.0	28.6	84	>99	Powder
12	12.8K, 1.56, 8:92	160.1	10.1	41.4	71	94	Powder
13	16.5K, 1.49, 8:92	169.1	-	-	78	95	Powder

Polymerisation conditions: $scCO_2$ polymerisation at 35 °C for 48 hours with V-70 initiator and 5 wt % of stabiliser. [a]Stabiliser M_n and PDI determined *via* GPC-RI with THF eluent and PS standards, Ratio determined from ^{1}H NMR. [b]Stabiliser cloud point determined using variable volume view cell. [c]Mean particle diameter as determined from sampling of ~100 particles of a typical SEM image. [d]Coefficient of variance as determined by equation $C_v = (\sigma/D_n) \times 100$. [e]Yield determined gravimetrically. [f]Conversion determined from ^{1}H NMR in $CDCl_3$.

In addition, DeSimone *et al.* showed that the rate of decomposition of AIBN in $scCO_2$ was 2.5 times lower than in the equivalent reactions in benzene.[35] Therefore, employing a relatively high initiator loading during the polymerisations in $scCO_2$ also aims to combat this and ensure reasonable radical generation, and sufficient initiation of all growing polymer chains at the start of the reaction.

As expected, the PNVP products appear to be polydisperse with relatively high molecular weights. The observed PDI was broad for a typical free radical polymerisation (4.1-6.1), but these results are consistent with those of PNVP dispersions in $scCO_2$ by Berger *et al.*, where M_w = 250 kg/mol and PDI = 9.7.[26] The unusually high polydispersity was attributed by these authors to inhomogeneous, non-stationary reaction conditions, and a high radical transfer rate to monomer.

The conversion of the polymers was obtained from ^1H NMR of the final product to establish the presence of remaining monomer within the sample (Figure 4.11). Yield was determined gravimetrically, weighing the polymer product obtained after drying overnight in a vacuum.

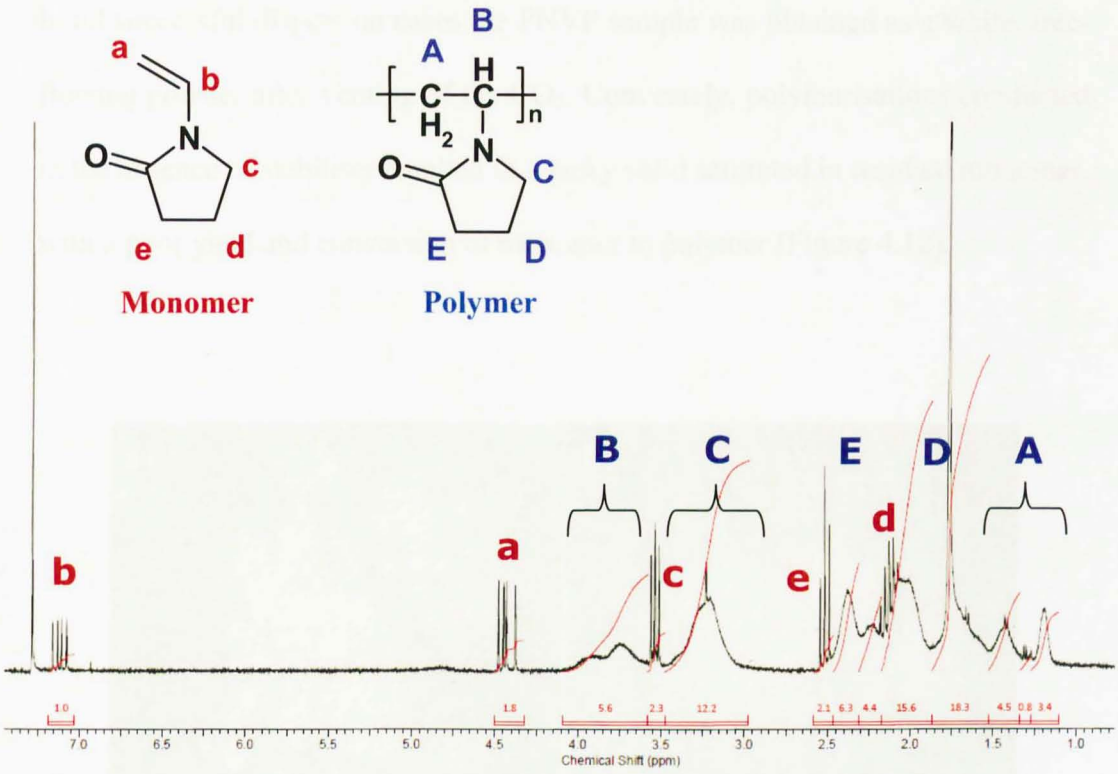


Figure 4.11: ^{1}H NMR of polymer + monomer from PNVP dispersion polymerisation in $scCO_2$. Conversion determined from comparison of integrals of monomer peak b with corresponding polymer peak B.

All of the polymerisations using the PVPi-based stabilisers exhibited high yield and conversion. It is important to note that venting of the CO_2 from the reaction vessel ultimately results in loss of the monomer, and as a result all conversions will typically appear high. To account for any inaccuracies in the determination of conversion as a result of the venting process, the yield will be considered for comparison of the polymerisation products rather than conversion.

In all successful dispersion cases the PNVP sample was obtained as a white, free-flowing powder after venting of the CO_2. Conversely, polymerisations conducted in the absence of stabiliser resulted in a tacky solid saturated in residual monomer, with a poor yield and conversion of monomer to polymer (Figure 4.12).

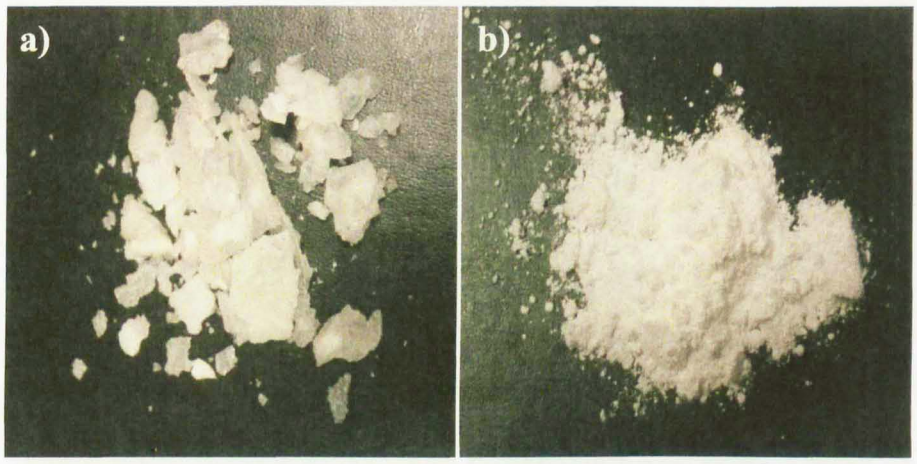


Figure 4.12: PNVP products obtained from polymerisation in $scCO_2$. (a) Product of unsuccessful dispersion gives a tacky solid/monomer mixture with no defined particle morphology; (b) PNVP product obtained from successful dispersion in the form of a fine, white, free-flowing powder;

Stabilising ability can be compared in more depth upon analysis and comparison of the SEM images and considering in detail the particle morphology and particle size diameter of the products obtained.

4.3.1.1 Variation of Homopolymer Stabiliser Molecular Weight

Initially the PVPi homopolymers were applied in the polymerisation in NVP in $scCO_2$. The results of the polymerisation were characterised *via* SEM (Figure 4.13).

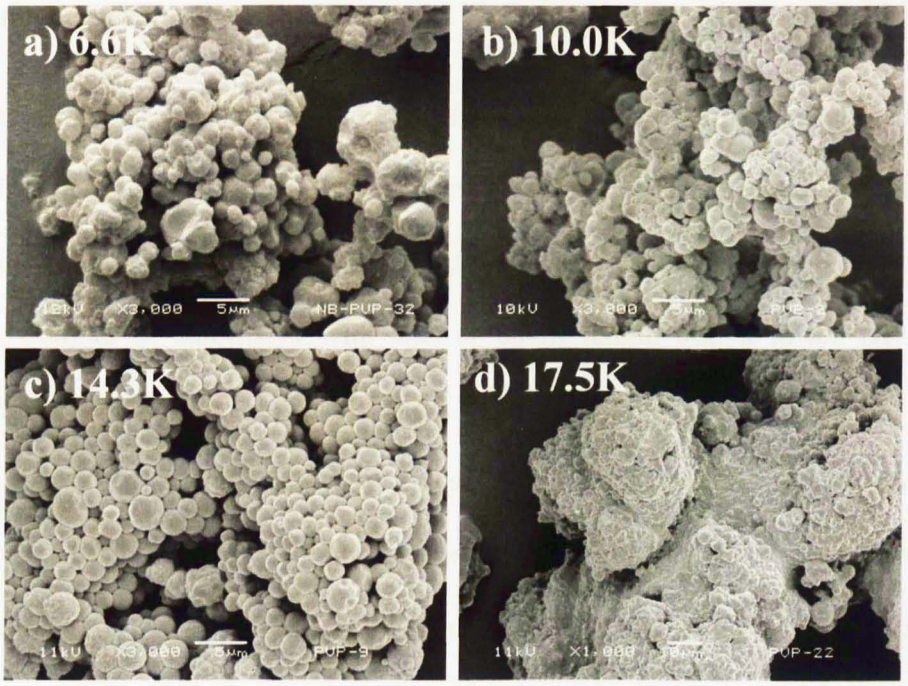


Figure 4.13: Variation of PNVP particle morphology with homopolymer stabiliser molecular weight. (a) 6.6K ; (b) 10.0K; (c) 14.3K; (d) 17.5K.

When employing the PVPi homopolymer stabilisers in dispersion polymerisation (Table 4.1; entries 1 and 2) a white, powder product with high yield was obtained.

At low molecular weight of 6.6K, particle morphology was ill-defined and irregular, although there was some indication of the formation of spherical microparticles (Figure 4.13, a). This observation can be attributed to the insufficient length of the stabiliser at this molecular weight, resulting in poor steric stabilisation and a poorly stabilised dispersion polymerisation. A 10.0K stabiliser resulted in PNVP product with some spherical particle formation, although the spheres were ill-defined and highly agglomerated (Figure 4.13, b).

As the molecular weight of the stabiliser was increased to 14.3K, distinct, spherical particle morphology was observed, indicating the increasing molecular weight gave sufficient length to provide adequate steric stabilisation (Figure 4.13, c). In Chapter 3, stabilisers with shorter chain length and a lower DP were determined to be more soluble in CO_2 (Chapter 3, Figure 4.4, a). However, these stabilisers were not as effective in subsequent dispersion polymerisations, presumably because they do not possess a sufficient chain length to provide adequate steric stabilisation. With too short a chain length, the polymeric surfactant will be unable to generate sufficient repulsive force to keep the individual growing polymer particles apart. The attractive Van der Waals interactions between the particles will dominate and this will allow aggregation to take place.[36-38]

However, as the molecular weight was increased further, to 17.5K, there appeared to be no control over particle morphology, resulting in an agglomerated mass (Figure 4.13, d). This suggests that at this molecular weight, the stabiliser possesses a sufficiently long backbone to force steric stabilisation and aid in

dispersion polymerisation to produce a high yielding powder product, but as a result of this chain length, the stabiliser is not soluble enough in $scCO_2$ to allow for an effective dispersion polymerisation, leading to a poorer particle morphology in such cases. Additionally, employing the same weight percentage of a higher molecular weight stabiliser will ultimately result in fewer chains in the polymerisation medium. Therefore, there is also a lower concentration of xanthate chain ends present. Consequently , if it is assumed that the xanthate end-group is required to adhere and anchor to the growing PNVP particle, fewer anchor points are available to graft to the growing polymer chain in $scCO_2$, leading to poorer surface coverage and insufficient stabilisation.

4.3.1.2 Variation of Copolymer Stabiliser Composition

Following the successful polymerisations in $scCO_2$ using the homopolymers, a series of the PVAc-*s*-PVPi-X copolymers (~10 kg/mol) were employed in high pressure reactions using NVP as the monomer (Table 4.1; entries 3-7).

All polymerisations resulted in a free-flowing powder product and high yield. SEM images again indicated the production of distinct particles, with variation in the average particle diameter. All particles exhibited some agglomeration, which can be ascribed to plasticisation of the PNVP shells in $scCO_2$.[26]

In comparison to the PVPi homopolymer stabilisers, the PNVP product obtained from dispersion using copolymer stabilisers exhibited a marked improvement (Figure 4.14).

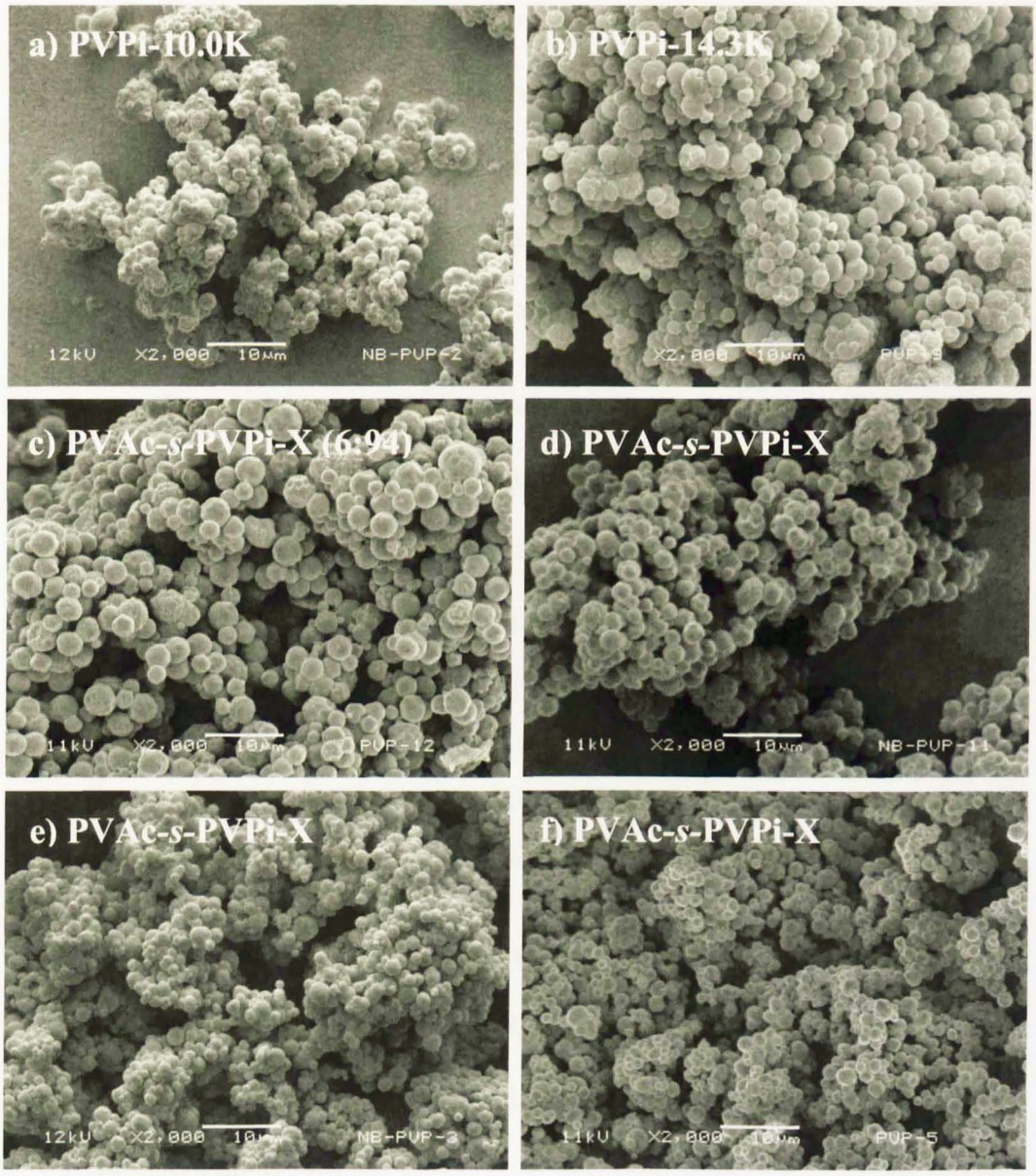


Figure 4.14: SEM analysis of effect on particle morphology with variation of copolymer composition at 5 wt % stabiliser loading w.r.t monomer: (a) PVPi 10.0K; (b) PVPi 14.3K; (c) PVAc-*s*-PVPi 6:94; (d) PVAc-*s*-PVPi 16:84; (e) PVAc-*s*-PVPi 24:76; (f) PVAc-*s*-PVPi 44:56. Note there is a clear decrease in particle size at increased VAc ratio (Table 4.1; entries 3-7). PVPi homopolymers are shown for direct comparison.

Further, variation in the copolymer composition was observed to have an effect on the particle morphology. Stabilisers with a very low proportion of VAc residues (6:94 and 16:84) resulted in spherical particle morphology (Figure 4.14, c-d). When the composition was adjusted, and 44:56 PVAc:PVPi stabiliser was employed, a decrease in the size of the particles was observed (Figure 4.14, f).

It appears that particles are smaller and more spherical as the PVAc content incorporated into the stabiliser is increased. The mean particle diameter highlights the differences between the stabilisers with varying compositions, in which as the proportion of VAc increases the particle size is reduced (Table 4.1, entries 3-7, column 7). The particle size distribution remains largely similar for the range of compositions, although is observed to be broader for PVPi-X equivalents (10.0K).

The findings described in this section can be summarised as follows:

1. Statistical copolymer structures are more successful at supporting dispersion polymerisations in $scCO_2$, possessing improved solubility and particle morphology control in dispersion polymerisations relative to the homopolymers.
2. A larger proportion of VPi/smaller proportion of VAc in the copolymer stabiliser structure will result in improved CO_2-solubility as a result of increased free volume.
3. Conversely, a larger proportion of VAc in the copolymer structure produces smaller PNVP particles in dispersion polymerisations.

These observations show that, coupled with the improved solubility of copolymers in comparison to homopolymers highlighted in the phase behaviour studies in Chapter 3, it is evident that copolymers are more suitable as stabilisers for PNVP. Particle morphology trends observed from the SEM micrographs suggest that although stabilisers with a lower VAc content in their composition are most soluble in CO_2, these stabilisers also result in increased particle size.

There are a number of explanations for this. Whilst VPi affords a stabiliser with a high free volume, and therefore reduced polymer-polymer interactions, a certain proportion of VAc is clearly required to provide increased flexibility to the polymer, improving dissolution in $scCO_2$ further.

As there appears to be a relationship between particle size and copolymer composition, it is also possible that if the stabilisers are anchoring *via* a physical mechanism (Figure 4.10, b) and one of the monomers (*e.g.* VAc) could potentially possess a better affinity for anchoring to the stabiliser. If this is the case, then it would be expected that a particular amount of this monomer within the stabiliser will be required to afford sufficient anchoring to the polymer particle surface and to achieve subsequent stabilisation.

The differences in particle size with stabiliser composition may also be explained by alterations in the partitioning of the stabiliser at the particle surface. With too high a proportion of VPi, the stabiliser will be much more soluble in the continuous phase, and show a decreased affinity for the growing PNVP polymer particle.

Overall, these findings suggest that solubility is not the sole factor to consider when determining the most suitable surfactant for dispersions, and phase behaviour measurements alone are not enough to determine the stabilising ability of a material.

4.3.1.3 Effect of Copolymer Molecular Weight

A molecular weight study of stabiliser materials was carried out. Both ~50:50 and 10:90 PVAc:PVPi ratios were studied (Table 4.2; entries 1-8 and 9-13 respectively).

Initially the 50:50 PVAc:PVPi ratio was considered, with molecular weights ranging from 4.7K to 29.4K (Figure 4.15, a-f).

In the case of the 50:50 ratio, no spherical particle formation was observed using a 4.7K stabiliser, and a hard solid was obtained, indicating dispersion polymerisation was unsuccessful in this case (Figure 4.15, a). Another low molecular weight stabiliser of 5.7K led to the production of PNVP powder in high yield, but the chain length is insufficient to force sufficient steric stabilisation and control the particle morphology to any great extent. Thus, the resulting particles are ill-defined and highly agglomerated.

As the molecular weight of the stabiliser is increased, PNVP particles of increasing particle diameter are produced and at 21.8K, the size of the particles of PNVP are significantly larger (Figure 4.15, b-e). There also appears to be a limit

at ~29K where powder product is no longer produced and control over particle morphology is lost (Figure 4.15, f).

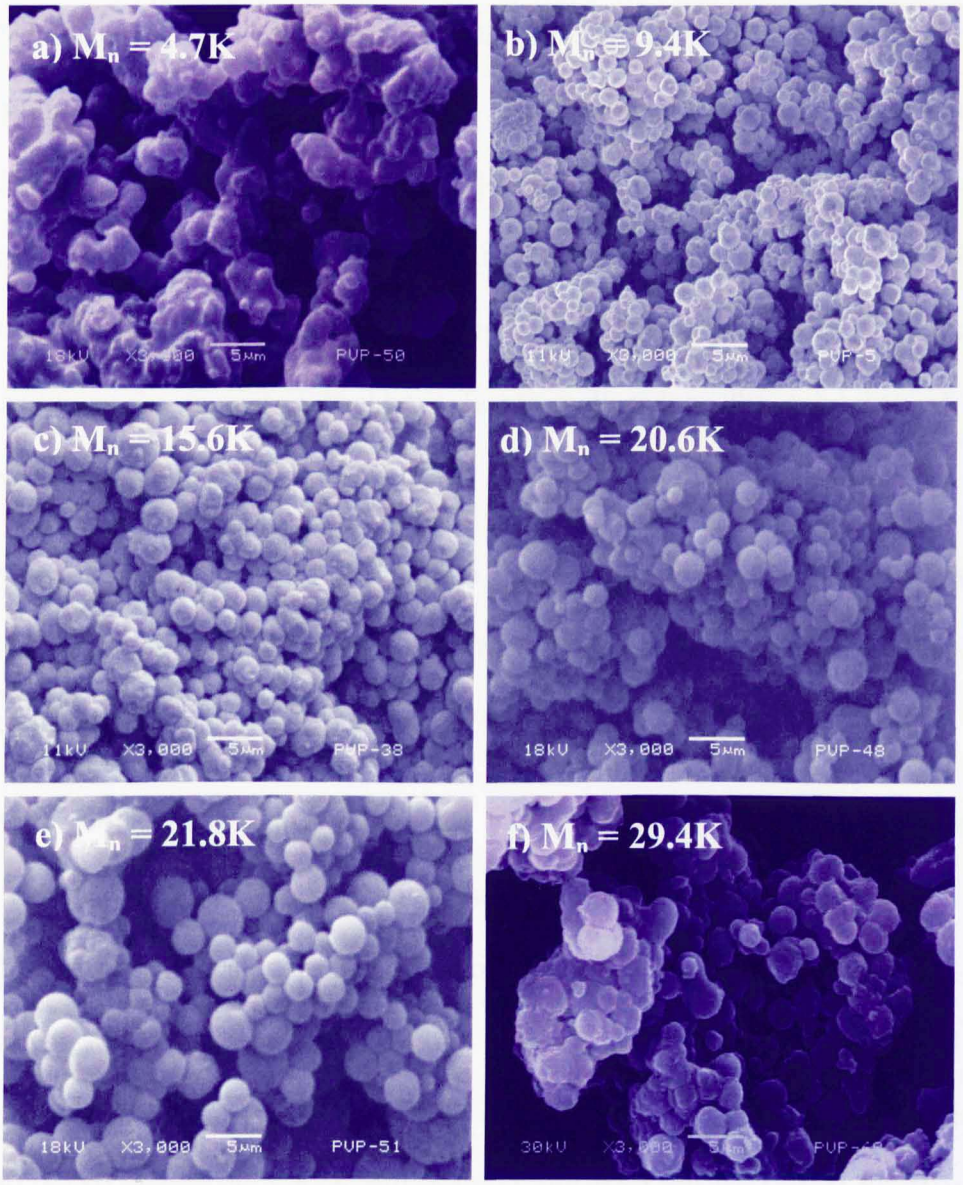


Figure 4.15: Variation of particle morphology with different molecular weight stabilisers of 50:50 ratio (Table 4.2; entries 1-3, 5-6): (a) M_n= 4.7K; (b) M_n= 9.4K; (c) M_n= 15.6K; (d) M_n= 20.6K; (e) M_n= 21.8K; (f) M_n=29.4K.

Studies on stabiliser molecular weight by DeSimone *et al.* led to the conclusion that increasing the molecular weight of the stabiliser resulted in larger particles.[39] Such observations have been confirmed in our studies using the PVPi-based stabilisers, as the average particle size diameter increases with increasing molecular weight and backbone length of the stabiliser (Table 4.2, entries 1-8, column 4). As in the case of the PVPi-X homopolymer stabilisers, this can be attributed to the presence of fewer molecules at higher molecular weight, and therefore a decreased proportion of xanthate chain ends for grafting to the PNVP particles, leading to decreased surface coverage and subsequently larger particles. In addition, the increased backbone length will reduce the solubility of the stabiliser in $scCO_2$.

Polymerisation using a set of 10:90 ratio stabilisers have also been characterised, and the range of molecular weights at which these stabilisers can be employed is much more restricted (Table 4.2, entries 9-13).

The low molecular weight limits of the 10:90 stabilisers appear to be similar to those of the 50:50 stabilisers. In both cases, a stabiliser of ~ 10.0K is required for well-defined, spherical particle formation (Figure 4.15, b and Figure 4.16, c). However, the upper molecular weight limit is much lower, with control of spherical particle morphology being lost at 12.8K (Figure 4.16, d), in comparison to the 50:50 stabilisers, which still produce spherical particles at 21.8K (Figure 4.15, e).

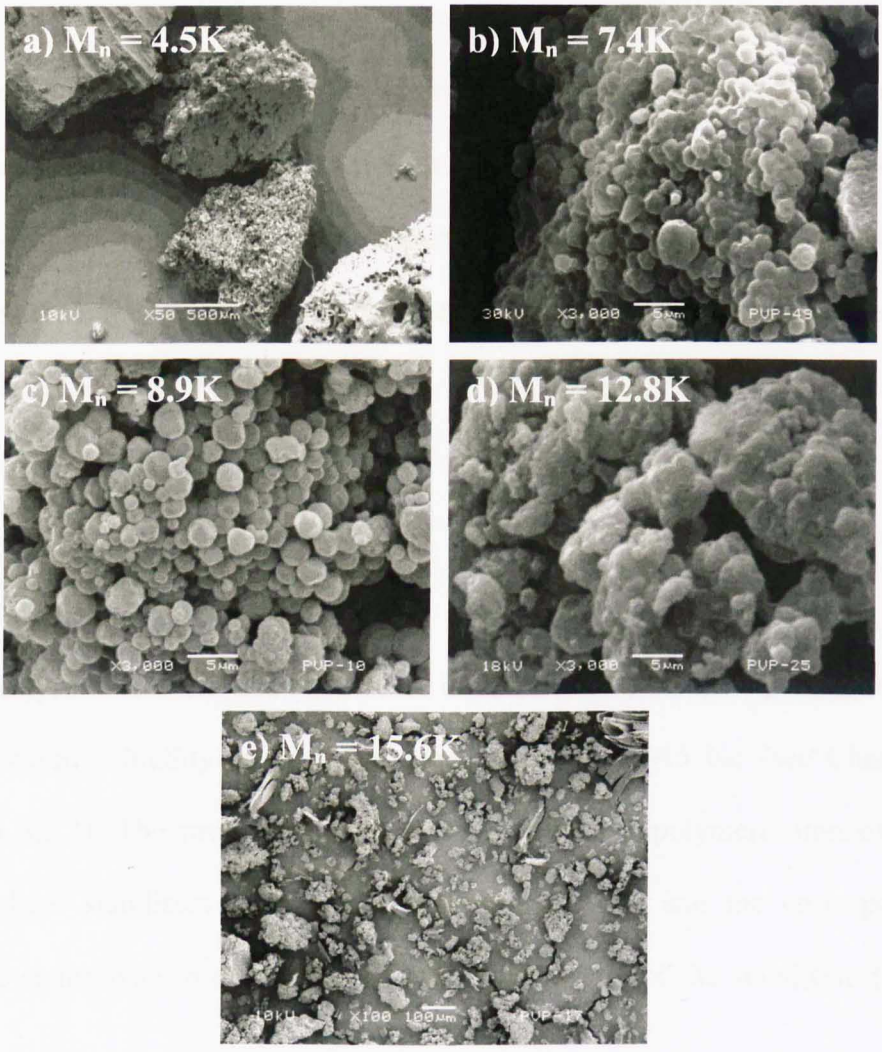


Figure 4.16: Variation of particle morphology with different molecular weight copolymer stabilisers of 10:90 ratio (Table 4.2; entries 9-12): (a) M_n= 4.5K; (b) M_n= 7.4K (c) M_n= 8.9K; (d) M_n= 12.8K; (e) M_n=15.6K.

It is clear from these results that in addition to producing smaller particles and a more spherical morphology, the stabilisers with a greater proportion of PVPi also have a wider molecular weight range at which they can operate successfully. Despite the stabilisers with a higher proportion of PVPi being more soluble in

CO_2, overall they appear to be less successful at stabilising dispersion polymerisations of NVP. A sufficient proportion of PVAc within the copolymer structure is required. This correlates with the observations made in section 4.3.1.2. One reason for this could be the additional flexibility conferred by incorporating VAc within the structure, allowing for improved interaction with $scCO_2$, optimising the activity of the stabilisers.

4.3.1.4 PDI Effect

Previously, it was noted that an increase in PDI of ~0.15 for the stabiliser resulted in decreased solubility and a cloud point increase of ~15 bar (see Chapter 3, section 3.2.3). The products obtained from dispersion polymerisation of NVP using these stabilisers were also compared *via* SEM and the corresponding particle sizing data to determine the effect of the PDI of the stabilisers (Figure 4.17).

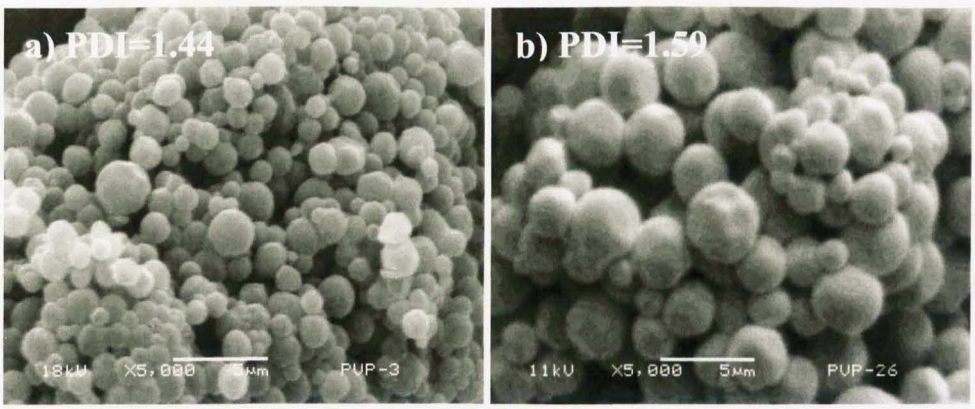


Figure 4.17: Effect of particle morphology with varying stabiliser PDI. (a) PDI = 1.44 (b) PDI = 1.59.

All PVP products were obtained in the form of free flowing, powder products. The SEM images show that despite the PDI difference, spherical particle morphology is obtained in both cases. There does appear to be some variation, with an increase in the average particle size for the case of the higher PDI equivalent. Particle sizing indicates that a PDI of 1.44 gives a mean particle diameter of 1.9 μm, whilst a broader PDI of 1.59 gives a larger mean particle diameter of 3.3 μm (Table 4.4). The distribution of particle size diameters, as evidenced by the C_v, appears to be very similar, indicating that the PDI had no appreciable effect on this parameter.

Table 4.4: Variation of PDI of PVAc-*s*-PVPi-X stabiliser.

Stabiliser		PVP Product				
Details (M_n, PDI, ratio)	**Cloud Point (psi)[a]**	**M_w(kg/mol)[b]**	**PDI[b]**	**D_n (μm)[c]**	**Cv (%)[d]**	**Yield (%)[e]**
10.3K, 1.44, 24:76	144.8	219	4.7	1.9	28.0	90
10.1K, 1.59, 24:76	159.0	216	6.1	3.3	30.1	85

Polymerisation conditions: $scCO_2$ polymerisation at 35 °C for 48 hours with V-70 initiator. [a]Cloud point pressure determined at 35 °C using variable volume view cell. [b]Experimental M_w and PDI obtained from GPC-RI detector in chloroform with 5 % triethylamine using PS standards. [c]Mean particle diameter as determined from sampling of ~100 particles of a typical SEM image. [d]Coefficient of variance as determined by equation $C_v = (\sigma/D_n) \times 100$. [e]Yield determined gravimetrically.

Overall, results of the PDI comparison indicate that a broad PDI polymer will produce larger particles (Figure 4.17, a-b and Table 4.4). The fraction of polymer chains within the sample which are optimum molecular weight for stabilisation will be decreased when an increasingly polydisperse surfactant is employed. This could be the reason for the larger particles produced with broader stabiliser PDI, as the effective steric stabilisation is reduced. The surface coverage of the growing PNVP particles will be less effective, and as less surface area is stabilised, larger particles are produced. Ideally, a narrow PDI is required for successful stabilisation using the PVAc-*s*-PVPi-X stabilisers, which is achieved successfully using the RAFT polymerisation technique.

4.3.1.5 Variation of Stabiliser Concentration

A study on the effect of the weight percentage of stabiliser employed in $scCO_2$ reactions was carried out to determine the effect of stabiliser loading on the product of polymerisation (Figure 4.18). The stabiliser used for this study was PVAc-*s*-PVPi-X (9.4K, 1.50, 44:56), which we have established to stabilise successfully at 5 wt % (figure 4.18, b).

Three additional stabiliser loadings were used, and SEM micrographs were obtained for all PNVP products. All weight percentages of stabiliser gave a white, free flowing powder at high yield, but the SEM data showed some variation in the particle morphology. At a very low level of 2.0 wt %, only highly distorted near-spherical structures of >10 μm were produced (Figure 4.18, a).

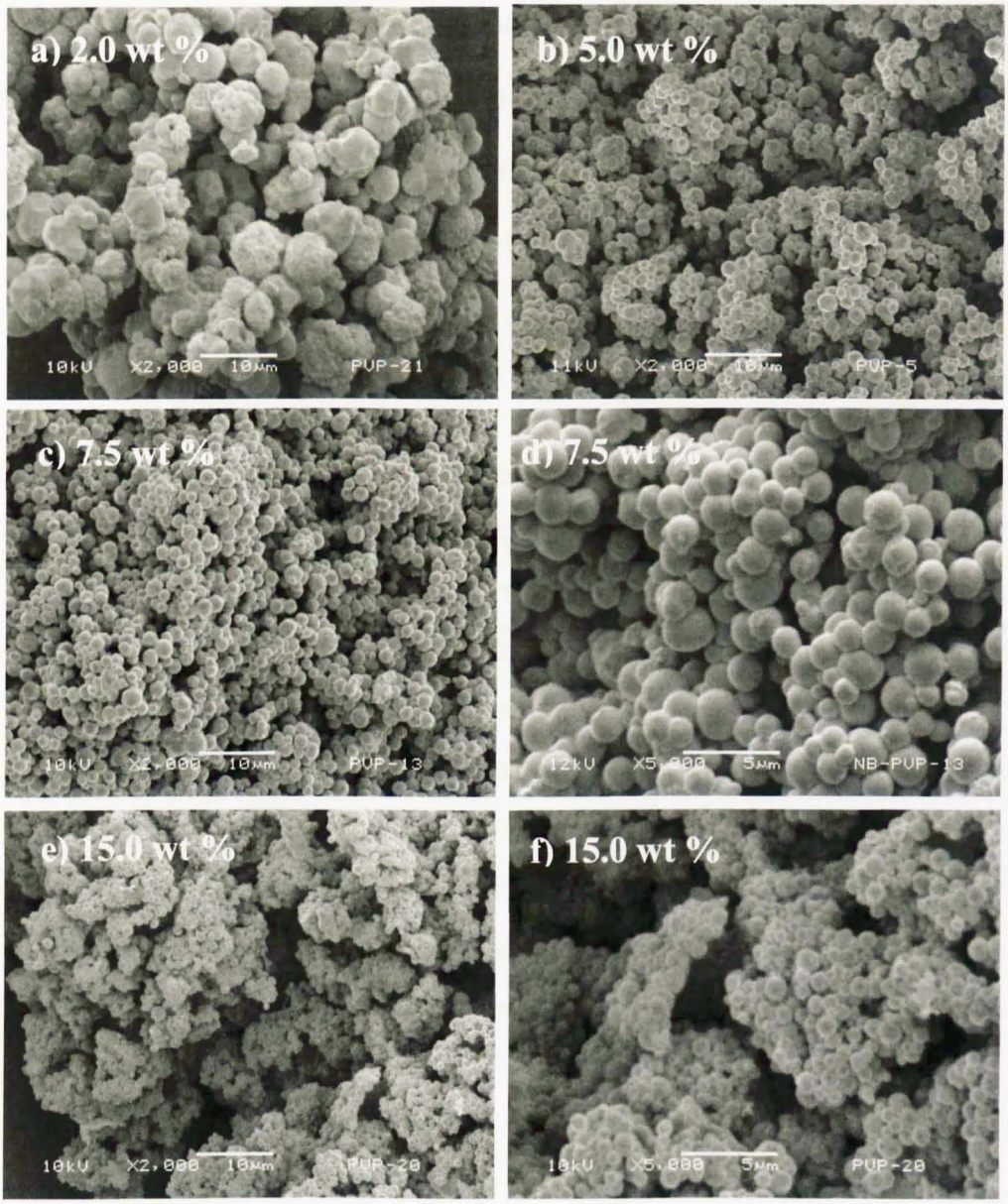


Figure 4.18: Variation of weight percentage of stabiliser: (a) 2.0 wt %; (b) 5 wt %; (c) 7.5 wt % at 2000 magnification (d) 7.5 wt % at 5000 magnification (e) 15.0 wt % at 2000 magnification and (f) 15.0 wt % at 5000 magnification. Particles are well defined and spherical at 5 wt %, and there is a reduction in particle size as wt % is increased. Data obtained from Table 4.5, entries 1-4.

The effect of using such a low proportion of surfactant material indicates there is insufficient stabiliser present to obtain well defined particle morphology. At higher levels, spherical particles were obtained up to 15.0 wt % with average diameter < 1 μm in size (Figures 4.18; b-f and Table 4.5).

Table 4.5: Variation of Stabiliser Weight Percentage.

Stabiliser wt %	PNVP D_n (μm)[a]	PNVP C_V (%)[b]	PNVP Yield (%)[c]	PNVP Appearance
2.0	4.2	28.9	83	Powder
5.0	1.4	30.2	86	Powder
7.5	1.3	27.0	85	Powder
15.0	0.7	29.0	79	Powder

Polymerisation conditions: $scCO_2$ polymerisation at 35 °C for 48 hours with V-70 initiator. [a]Mean particle diameter as determined from sampling of ~100 particles of a typical SEM image. [b]Coefficient of variance as determined by equation $C_v = (\sigma/D_n) \times 100$. [c]Yield determined gravimetrically.

The particle sizing data show a clear reduction in particle size diameter as the percentage stabiliser is increased (Table 4.5). As observed in similar studies of surfactant concentration in dispersion systems, increasing concentrations of stabiliser result in a greater surface area of polymer potentially being coordinated to stabiliser molecules, which leads to a reduction in the particle size of the final product.[37, 40-43] During the nucleation period, nuclei are formed and as the particles precipitate, are captured and supported by the stabiliser chains, allowing

for particle growth. As the concentration of stabiliser is increased, a larger number of nuclei are produced, and smaller particles obtained.

As mentioned, numerous groups have considered the effect of stabiliser concentration on dispersion polymerisation. Canelas *et al.* reported the dispersion polymerisation of styrene in $scCO_2$ using a PS-*b*-PDMS stabiliser. As the stabiliser was varied from 2.0 to 15.0 wt %, the particle size decreased from 1.15 to 0.31 μm.[42] Similarly, in dispersion polymerisations of PNVP carried out in the DeSimone group using PFOA as a surfactant, as the concentration of the stabiliser employed was increased from 0.25 to 6.0 wt %, the average particle size was again observed to decrease, in agreement with other studies.[25] This was also observed for MMA polymerisations, in which the concentration of PFOA was varied from 0 to 16.0 wt %, and the corresponding particle size diameter ranged from 2.86 to 1.55 μm (Figure 4.19).[41]

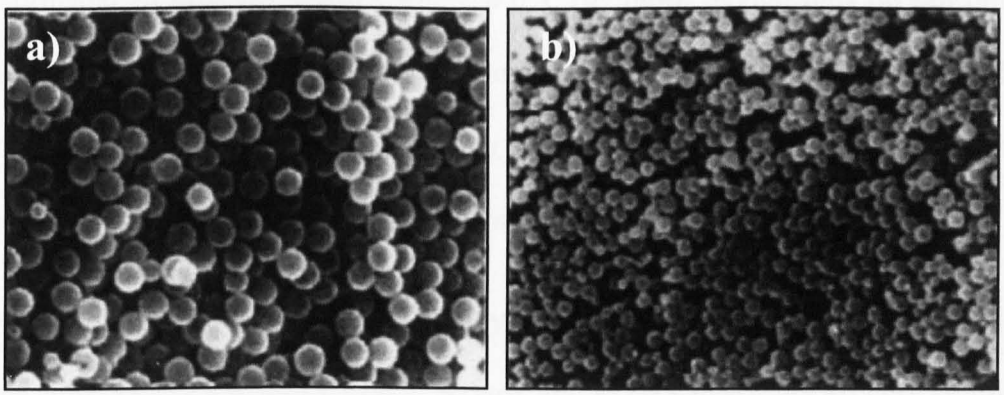


Figure 4.19: SEM micrographs of PMMA latex particles synthesised by DeSimone *et al.* using PFOA surfactant at a) 2.3 wt % and b) 16 wt %.[41]

Similar effects have also been observed in conventional organic solvents. For example, Shen *et al.* carried out a study of the dispersion polymerisation of MMA in methanol, and clearly demonstrated a decrease in particle size as the concentration of the stabiliser was increased.[43]

The "gold standard" for stabilisers or dispersants in $scCO_2$ has always been highly soluble fluorinated stabilisers such as Krytox 157-FSL and PFOA. These stabilisers allow for the synthesis of highly spherical, micron-sized particles with high conversion of monomer to polymer, and have been reported to stabilise dispersion polymerisations of PMMA and enable the formation of discrete particles at stabiliser concentrations as low as 1.0 wt % and 0.24 wt% respectively.

However, when converted to molar concentrations it becomes clear that the poly(vinyl alkanoates) are performing at a promising level. For example at 5 wt % (4.5×10^{-5} mol) the poly(vinyl alkanoates) are approaching equivalence with the fluorinated Krytox-157 FSL (1 wt %; 4.0×10^{-5} mol), though they do not quite match the extremely low concentrations reported for PFOA.[41] Moreover, the poly(vinyl alkanoates) are performing as effectively as the more common methacrylate terminated silicone (10 kg/mol) (5 wt %; 4.0×10^{-5} mol).[44]

Despite the differences in wt % employed for all of these stabilisers, the molar concentrations of PVAc-*s*-PVPi-X, Krytox and PDMS-mMA are all very similar. This could indicate that sufficient surface coverage of the stabiliser is required to

function effectively, and although different stabiliser loadings in terms of wt % are employed, there is suitable surface coverage in all cases.

Clearly these findings demonstrate that inexpensive and environmentally acceptable hydrocarbon stabilisers for use in $scCO_2$ are now within reach using PVPi-based stabilisers (typically, Krytox 157-FSL = £827/Kg as supplied by DuPont, and PVPi = ~£58/Kg). Hydrocarbon stabilisers with high solubility will potentially allow polymerisations to be conducted at lower pressures, reducing the overall compression costs required. The use of less toxic alternatives to fluorinated materials as stabilisers could also be appealing in industrial applications. These materials could potentially overcome the reliance upon fluorinated or silicone containing polymers that have proven to be one of the major barriers to wider commercialisation.

4.3.1.6 Variation of Reaction Parameters

In order to assess how robust the stabilising ability of the polymers were to changes to the reaction conditions, a series of additional experiments were undertaken. The effect of reaction pressure, initiator loading, and reaction time was considered.

Polymerisation Reaction Pressure

The reaction pressure of the vessel, and therefore the density of CO_2 within the reaction, was adjusted in a set of 3 polymerisations. The same polymeric stabiliser (PVAc-*s*-PVPi-X; 12.1K, 1.46, 24:76) was employed in all cases and all other reaction parameters were also kept constant. The cloud point pressure at 35 °C for the stabiliser employed is 154 bar. Three polymerisation pressures were studied between 207 and 276 bar (Table 4.6).

The effect of pressure was considered using SEM. In all polymerisations, the stabiliser was soluble at the reaction pressures used. The effect of pressure appears to have little effect on the PNVP product obtained. Polymerisations at 276 and 241 bar both result in spherical microparticle formation and a high yield (Figure 4.20, a-b). The particle size diameter, D_n, was observed to increase slightly at the two lower pressure conditions. The coefficient of variance was calculated as ~20 to 30 % in all cases, indicating the distribution of particle sizes within the sample is relatively the same for all pressures tested.

Table 4.6: Polymerisation of NP at Varying Pressure.

Pressure (bar)	M_w (kg/mol)[a]	PDI[a]	D_n (μm)[b]	Cv (%)[c]	Yield (%)[d]	Appearance
276	223	4.3	2.1	23.2	89	Powder
241	270	5.2	2.5	19.8	83	Powder
207	282	5.2	2.5	27.2	93	Powder

Polymerisation conditions: $scCO_2$ polymerisation at 35 °C for 48 hours with V-70 initiator. [a]Experimental M_w and PDI obtained from GPC-RI detector in chloroform with 5 % triethylamine using PS standards. [b]Mean particle diameter as determined from sampling of ~100 particles of a typical SEM image. [c]Coefficient of variance as determined by equation $C_v = (\sigma/D_n) \times 100$. [d]Yield determined gravimetrically.

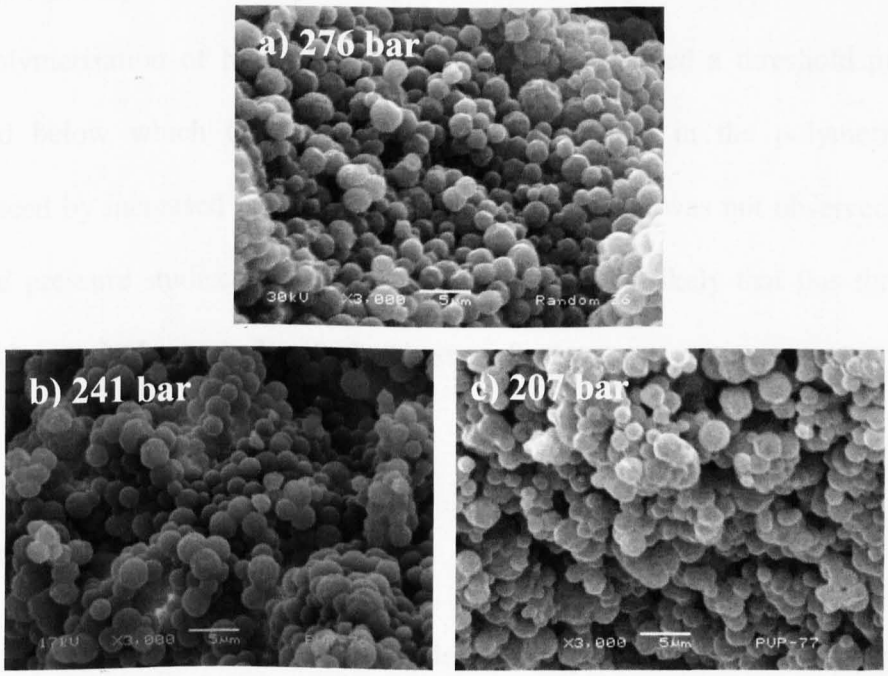


Figure 4.20: SEM micrographs obtained from PNVP polymerisation at varying reaction pressure using PVAc-*s*-PVPi-X stabiliser at 5 wt %. (a) 276 bar; (b) 241 bar; (c) 207 bar.

At 207 bar (Figure 4.20, c), despite the reduction in pressure and therefore reduced solvating power, the stabiliser is still able to successfully support a dispersion polymerisation, resulting in powder products with spherical particle morphology. It is important to note that these particles do appear to be slightly more agglomerated at 207 bar compared to those at higher pressure, although this is a visual, not quantitative, observation.

The results appear to agree with the findings of previous studies. Polymerisations of MMA with PFOA stabiliser were found to be insensitive to changes in pressure between 145 to 331 bar, producing latex particles of a similar diameter, molecular weight and yield.[41] Johnston *et al.* also found that particle size had no significant dependence on pressure above 3000 psi in a study using PDMS-mMA stabiliser in the polymerisation of MMA in CO_2.[45] The authors noted a threshold pressure existed below which there was a significant change in the polymerisation, evidenced by increased particle coagulation. Whilst this was not observed in the limited pressure studies carried out in this thesis, it is likely that this threshold would be reached upon reducing the pressure further.

Initiator Ratio

In all the polymerisation reactions described previously in this chapter, a stabiliser: initiator ratio of [1]:[10] was employed. In order to determine if there was any appreciable effect on particle morphology of the PNVP samples

synthesised from dispersion polymerisation, additional experiments were conducted with reduced initiator concentrations (Table 4.7).

Table 4.7: Adjustment of Initiator Ratio.

[S]:[I]	M_w (kg/mol)[a]	PDI[a]	D_n (μm)[b]	Cv (%)[c]	Yield (%)[d]	Appearance
1:10	223	4.3	2.1	23.2	89	Powder
1:1	301	4.1	3.3	22.3	87	Powder
2:1	167	3.0	-	-	78	Hard, Tacky Solid

Polymerisation conditions: $scCO_2$ polymerisation at 35 °C for 48 hours with V-70 initiator. [a]Experimental M_w and PDI obtained from GPC-RI detector in chloroform with 5 % triethylamine using PS standards. [b]Mean particle diameter as determined from sampling of ~100 particles of a typical SEM image. [c]Coefficient of variance as determined by equation $C_v = (\sigma/D_n) \times 100$. [d]Yield determined gravimetrically.

The PNVP products synthesised from the polymerisation reactions were obtained in a free-flowing powder form, with the exception of the reaction employing the lowest concentration of initiator, which resulted in a hard solid. The overall yield was also slightly reduced for this reaction. Increasing the initiator concentration in a polymerisation will generally lead to a decreased molecular weight because of a higher number of radicals within the system, and this is highlighted by the lower molecular weights obtained when employing increased initiator concentrations (Table 4.7, column 2). The unexpectedly low molecular weight of the PNVP product obtained at 2:1 stabiliser:initiator loading is attributed to the insolubility

of the very high molecular weight material, which was difficult to dissolve and filter during characterisation *via* GPC.

The SEM micrographs were compared to gauge the effect on particle morphology (Figure 4.21).

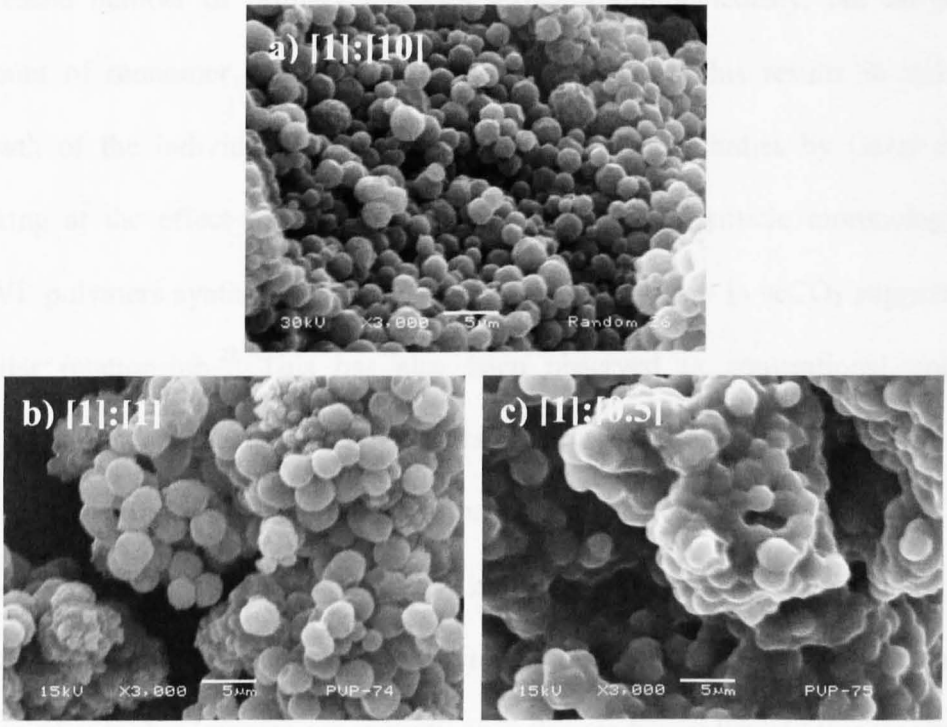


Figure 4.21: PNVP particle morphology obtained from polymerisation using different stabiliser to initiator loadings. (a) S:I = [1]:[10]; (b) S:I = [1]:[1]; (c) S:I = [1]:[0.5].

In the case of this study, the particle morphology was clearly affected, with the two higher initiator concentrations producing spherical particles, whilst the low level of initiator gave highly agglomerated structures which were very ill-defined,

showing some sign of spherical microparticle formation. Overall, an increase in D_n was observed as the initiator loading was decreased.

Typically, increasing the initiator concentration in a polymerisation will lead to a decreased particle size because more nucleation sites are formed and there are an increased number of primary particles growing simultaneously, but the same amount of monomer available in the polymerisation. This results in reduced growth of the individual primary particles.[37] Previous studies by Galia *et al.* looking at the effect of initiator concentration on the particle morphology of PNVP polymers synthesised *via* dispersion polymerisation in $scCO_2$ suggested a similar relationship.[28] This has also been observed in conventional organic solvents. Horak *et al.* found that a smaller particle morphology was observed with increasing initiator concentrations in the polymerisation of HEMA.[46] This was also observed by Capek *et al.* in the dispersion polymerisation of poly(oxyethylene methacrylate) with styrene.[47] A smaller particle size was indeed observed at higher initiator concentrations in this study, confirming this theory.

However, increased initiator concentration has also been observed to result in increased particle sizes in dispersion polymerisations. Studies have observed this trend, showing an increase in particle size as the initiator concentration was increased.[48, 49] This has been attributed to an increase in the free radical production rate, producing a greater instantaneous concentration of oligomeric radicals, which will in turn increase the association rate of the oligomers and the coagulation rate of the unstable nuclei. Ultimately this will result in the formation of larger particle nuclei.[50, 51] The impact of initiator concentration on the particle

size is assumed to be dependent on both the polymerisation system and the monomer employed.

Overall, based upon the limited experiments considered in this section, it appears that dispersion polymerisation of PNVP in $scCO_2$ with PVPi-based hydrocarbon stabilisers results in a decreased particle size as the initiator concentration is increased. Moreover, it is apparent that the initiator ratio can be successfully lowered to some extent, which is advantageous as less initiator material would be consumed in each reaction. However, too low a level of initiator leads to loss of control over the particle morphology and the appearance of the polymer.

Polymerisation Reaction Time

Previously, all high pressure polymerisation reactions were carried out over a period of 48 h. In order to determine if the reaction time could potentially be reduced, a polymerisation at 24 h was conducted. The PNVP product was analysed to determine if this reduction in polymerisation time had a significant effect on yield and particle morphology (Figure 4.22 and Table 4.8).

A free-flowing, powder product was obtained upon venting of the CO_2 and upon analysis of the SEM micrographs the particle morphology also appeared to be largely unaffected by the shorter reaction time, giving comparable spherical microparticles. The particle diameter remained largely unaffected despite reducing the reaction time by half. The C_v values were also similar, indicating no

distinct changes in particle size distribution. There was also no appreciable impact on the final yield or the overall molecular weight of the obtained PNVP product.

Table 4.8: Effect of Polymerisation Reaction Time.

Time (h)	M_w (kg/mol)[a]	PDI[a]	D_n (μm)[b]	Cv (%)[c]	Yield (%)[d]	Appearance
48	223	4.3	2.1	23.2	89	Powder
24	209	4.8	2.2	25.9	84	Powder

Polymerisation conditions: $scCO_2$ polymerisation at 35 °C for 48 hours with V-70 initiator. [a]Experimental M_w and PDI obtained from GPC-RI detector in chloroform with 5 % triethylamine using PS standards. [b]Mean particle diameter as determined from sampling of ~100 particles of a typical SEM image. [c]Coefficient of variance as determined by equation $C_v = (\sigma/D_n) \times 100$. [d]Yield determined gravimetrically.

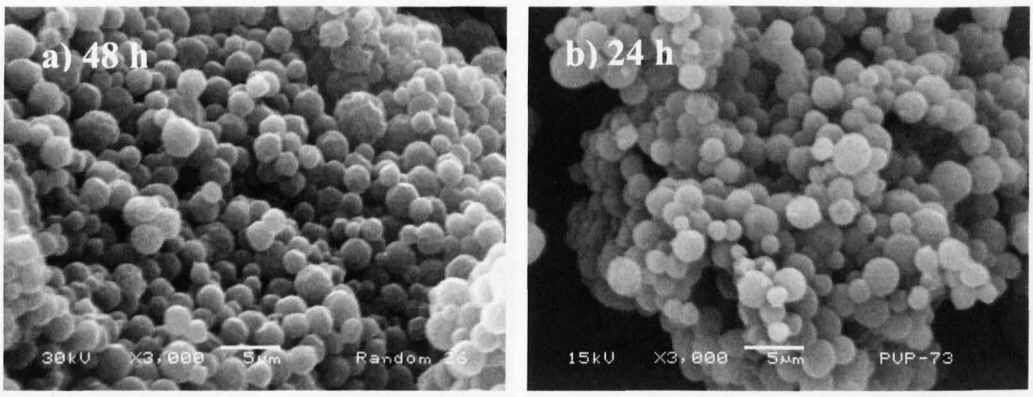


Figure 4.22: SEM micrographs of PNVP product from polymerisation at (a) 48 h and (b) 24 h.

These results demonstrate that the reaction time of the NVP polymerisations in $scCO_2$ can be minimised without any detrimental impact to the polymer product, in terms of both yield and particle size. Therefore, future polymerisations of PNVP in $scCO_2$ could successfully be carried out over a shorter period, potentially minimising the timescale of experiments and consequent energy costs of the reactions.

4.3.1.7 Investigation of New Monomer Alternatives

Monomers IPAc and VPr were polymerised with VPi using the RAFT polymerisation technique to produce statistical copolymer stabilisers. These stabilisers were then used for the polymerisation of NVP in $scCO_2$ (Figure 4.23).

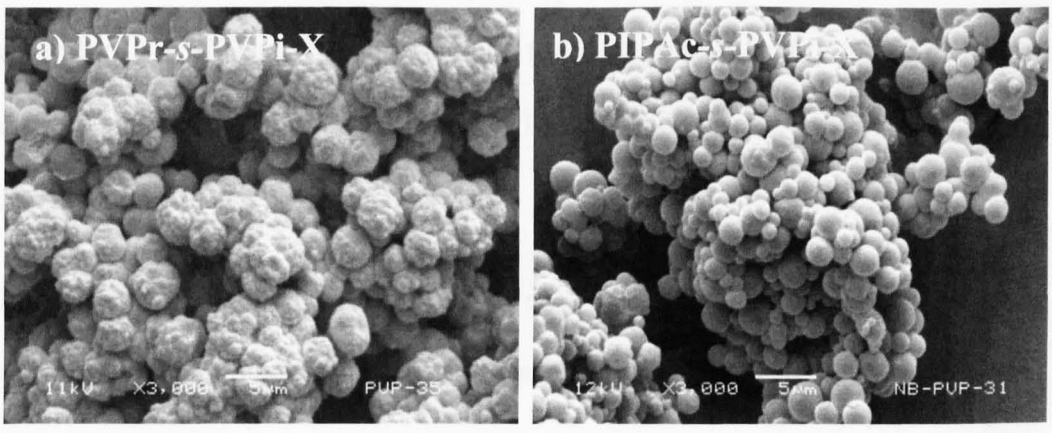


Figure 4.23: PNVP products using VPr and IPAc-based stabilisers. (a) PVPr-*s*-PVPi-X: 9.9K, 1.68, 25:75; (b) PIPAc-*s*-PVPi-X: 10.8K, 1.33, 17:83.

PVPr-*s*-PVPi-X used as a stabiliser gave PNVP products which indicated some form of spherical particle formation, but these particles are highly irregular. The PVPr-*s*-PVPi-X copolymer had poorer solubility than the PVAc-*s*-PVPi-X equivalent, so this is likely one of the reasons for the ill-defined particles. The PDI was also likely to have affected the particle morphology to some extent, being quite high when compared to the PIPAc equivalent (PDI = 1.68).

The PIPAc-*s*-PVPi-X copolymer gave much improved spherical particle formation, comparable to the PVAc-*s*-PVPi-X equivalent. PIPAc incorporated into the PVPi copolymer stabiliser was also found to have very similar solubility to the stabilisers produced when using VAc as a co-monomer. Therefore it is expected that the PNVP product would also be comparable. Overall however, this indicates there are no real advantages to employing IPAc as a co-monomer to replace VAc; solubility and product particle morphology is very similar, but polymerisation of IPAc is limited to copolymers with low proportions of IPAc as a result of the difficulty in polymerising the monomer. In addition, IPAc is much more expensive to purchase (IPAc = £120/Kg and VAc = £18/Kg as obtained from Sigma Aldrich chemical suppliers).

In conclusion, although IPAc and VPr were interesting alternatives to consider as co-monomers, both have no clear advantages compared to VAc.

4.3.1.8 Free Radical Copolymers as Stabilisers

To determine the requirement for RAFT polymerisation in the development of the PVPi-based hydrocarbon stabilisers, a copolymer stabiliser was synthesised *via* free radical polymerisation (Chapter 3). Following phase behaviour studies, dispersion polymerisations in $scCO_2$ using NVP monomer were conducted to compare the activity of the two stabilisers (Table 4.9 and Figure 4.24).

The free radical copolymer, PVAc-*s*-PVPi, was unsuccessful in producing a dispersion polymerisation, and upon venting of the high pressure vessel a hard, tacky solid was obtained with low PNVP yield. SEM micrographs also confirm this, and a highly agglomerated, irregular mass of PNVP is produced using the free radical stabiliser. This is a distinct contrast to the polymerisation employing the RAFT synthesised copolymer, in which a high yielding PNVP powder with spherical microparticle formation is obtained.

Table 4.9: Dispersion Polymerisation using Free Radical Copolymer Stabiliser.

Stabiliser	Stabiliser Details (M_n, PDI, ratio)	Cloud Point (bar)[a]	PNVP Yield (%)[b]	PNVP Appearance
PVAc-*s*-PVPi-FRP	10.0K, 2.05, 29:71	252.1	53	Hard Solid
PVAc-*s*-PVPi-X	10.3K, 1.44, 24:76	144.8	86	Powder

Polymerisation conditions: $scCO_2$ polymerisation at 35 °C for 48 hours with V-70 initiator. [a]Cloud point pressure determined at 35 °C using variable volume view cell. [b]Yield determined gravimetrically.

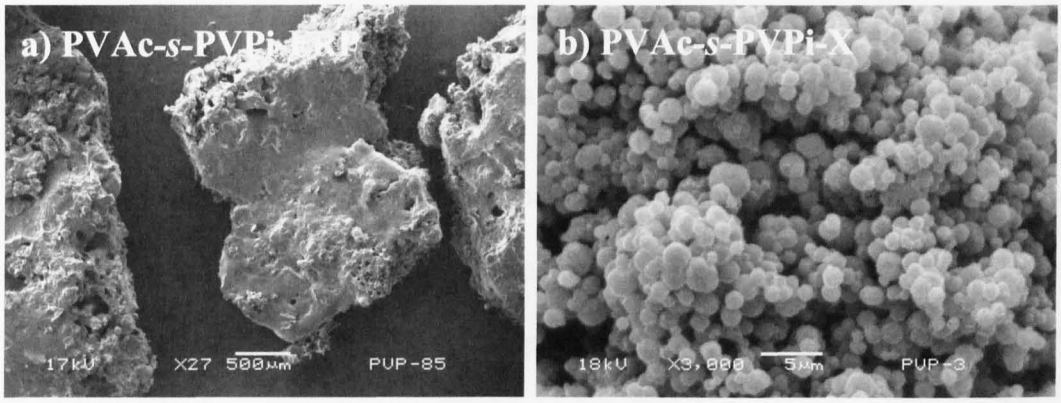


Figure 4.24: Comparison of PNVP products obtained from dispersion polymerisation using PVAc-*s*-PVPi-FRP copolymer synthesised by free radical polymerisation and PVAc-*s*-PVPi-X copolymer synthesised by RAFT polymerisation. (a) PVAc-*s*-PVPi 10.0K, 2.05, 29:71; (b) PVAc-*s*-PVPi-X 10.3K, 1.44, 24:76.

There are two key reasons why the free radical copolymer is potentially unable to act as an efficient stabiliser:

Firstly, a polymer-philic anchor group is a necessity for successful polymerisation of NVP in $scCO_2$. Without the presence of the stabiliser end-groups provided by the RAFT polymerisation mechanism, it is likely that dispersion polymerisation using the free radical synthesised stabiliser is unsuccessful as there is no way in which the stabiliser can graft to the growing PNVP particles in $scCO_2$. RAFT polymerisation is required in this case to provide a suitable anchor group, and without the presence of the xanthate chain the PVPi-based polymers cannot graft

and are unable to support the dispersion polymerisation in $scCO_2$. This requirement is investigated further in this thesis in Chapter 5.

Secondly, the free radical polymer has a much broader molecular weight distribution, and as such, will possess a range of molecular weights within the sample. Consequently, only a small proportion of the stabiliser material is likely to be of sufficient length to act as an adequate stabiliser and provide suitable stabilisation. Decreased steric stabilisation, reduced solubility and inadequate surface coverage as a result of this broad molecular weight distribution will all contribute to an ineffective stabilisation.

Comparison of PVAc-*s*-PVPi and PVAc-*s*-PVPi-X has demonstrated that controlled methods, such as RAFT polymerisation, provide a means of improving the solubility of stabilisers by accessing polymers with a narrow PDI, and enable a xanthate functionality to be incorporated into the structure with the potential to act as a polymer-philic anchor group. These factors have been proven to have a significant impact on the stabilising ability and are crucial in providing a successful dispersion polymerisation system. Further studies on the effect of stabiliser anchor group will be discussed in Chapter 5.

4.3.2 Hydrocarbon Stabiliser Synthesis in $scCO_2$

Following the successful synthesis and application of PVPi-X homopolymer and copolymer hydrocarbon stabilisers in the dispersion polymerisation of NVP in $scCO_2$, and the CO_2-solubility of these materials in the reaction medium, it was assumed that such stabiliser materials could potentially also be produced in $scCO_2$. Such an alternative approach for hydrocarbon stabiliser synthesis would remove the need for potentially environmentally unfriendly solvents used in the polymerisation/purification processes. With this in mind, a series of experiments were conducted to determine the applicability of this approach.

Initially, copolymer stabilisers with a feed ratio of 50:50 VAc:VPi were targeted for synthesis, followed by attempts to synthesise PVPi-X homopolymers. The results of the high pressure polymerisations are highlighted (Table 4.10).

PVAc-*s*-PVPi-X copolymer synthesis met with only moderate success (Table 4.10; entries 1-2). After 48 h, a 4.4K copolymer was produced, but the proportion of PVAc within the material was negligible. Extending the reaction time further somewhat improved results, and a higher conversion was obtained, but the product was in the form of a tacky solid swollen with residual monomer, and there was only slight improvement in terms of the experimental monomer ratio.

Homopolymer synthesis of PVPi-X was also attempted (Table 4.10; entries 3-6). As with the copolymer synthesis, the molecular weight did not meet the targeted molecular weight. PDI was narrow in all cases, confirming controlled polymerisation *via* use of the xanthate RAFT agent. The reaction time and the

amount of initiator employed were adjusted to determine if this had an impact. Molecular weight and conversion both increased as the initiator concentration/reaction time were increased, indicating such adjustments did go some way to improving the polymer produced. However, the product obtained remained a mixture of solid and monomer in most cases. Also, molecular weights obtained agreed reasonably well when comparing the conversion and the targeted molecular weight, correlating with the observed data.

Table 4.10: Synthesis of hydrocarbon stabilisers in $scCO_2$.

Entry	Monomers	$M_{n,expt}$ (kg/mol)[a]	PDI[a]	Ratio[b]	Conv. (%)[b]	[R]:[I]	Time (h)	Appearance
1	PVAc/PVPi	4.4	1.52	6:94	44	2:1	48	Viscous Liquid
2		5.5	1.33	12:88	75	1:1	72	Tacky Solid
3		3.6	1.38	-	63	2:1	48	Solid/Monomer
4	PVPi	5.8	1.30	-	69	1:1	48	Solid/Monomer
5		5.3	1.37	-	69	1:2	48	Solid/Monomer
6		6.6	1.32	-	79	1:1	72	Powder

Polymerisation conditions: $scCO_2$ polymerisation at 65 °C with AIBN initiator. Theoretical molecular weight ($M_{n,th}$) of 10 kg/mol and feed ratio of 50:50 PVAc:PVPi targeted in all polymerisations. [a]Stabiliser M_n and PDI determined *via* GPC-RI with THF eluent and PS standards. [b]Ratio and conversion of monomer to polymer determined from ^1H NMR.

The main exception appeared to be in the case of the synthesis carried out with [R]:[I] of 1:1 and a polymerisation time of 72 h. The product obtained from this reaction was a white, powder product with reasonable molecular weight and PDI.

However, the conversion still did not meet the typical homopolymer conversions obtained from conventional PVPi synthesis, and monomer residue was still present in the final material. However, with further extraction using $scCO_2$, the monomer could be removed.

The key issue with synthesising hydrocarbon stabilisers in this manner seems to arise from the rate of polymerisation. The reaction is unable to reach targeted molecular weights, despite some of the polymerisations being carried out for up to 72 h. If the reaction were to be prolonged further, it is possible a higher conversion and molecular weight could likely be attained, but this does not seem practical when conventional polymerisations may be carried out for only a few hours to yield a PVPi-X homopolymer with high conversion and experimental M_n close to that of the target M_n (see Chapter 3).

One possible alternative would be to carry out the synthesis of the hydrocarbon stabilisers in $scCO_2$ at much higher monomer concentrations, thus reducing the effects of dilution within the reaction medium and improving the rate of reaction. This would effectively be a CO_2-expanded phase reaction, in which the polymer is obtained from large quantities of the liquid monomer expanded with dense CO_2. This could potentially result in much higher conversions, and therefore no monomer residue in the final product, in addition to molecular weights much closer to target molecular weight. The polymerisation reaction time would also be significantly reduced using this method.

Overall however, the results so far regarding hydrocarbon stabiliser synthesis have met with insufficient success. In all cases, conversions have not been particularly high, and monomer residue has been retained within the final sample, meaning purification steps will still be required post-polymerisation. This suggests that the conventional means of synthesising these materials in bulk/solution polymerisation, followed by precipitation in an anti-solvent for purification is the most suitable method, despite the need for solvents for the purification steps.

4.4 Conclusions

The main aim of this work was to demonstrate the effectiveness of stabilisers composed of PVAc and PVPi in supporting dispersion polymerisation of NVP in $scCO_2$. One of the key issues in the development of hydrocarbon stabilisers is the synthesis of materials which are sufficiently CO_2-soluble and provide adequate steric stabilisation.

Previously in Chapter 3, CO_2-philic polymers composed of VAc and VPi were identified with the potential to act as stabilisers in dispersion polymerisations in $scCO_2$. In this chapter, it has been established that the PVPi-based hydrocarbon stabilisers are indeed effective for NVP polymerisations, being both highly CO_2-soluble and possessing sufficient stabilising activity to produce fine, powder products with high yield and controlled particle morphology. The efficacy of these stabilisers can be attributed to the favourable structure, incorporating a high free volume, increased flexibility and the presence of carbonyl groups for specific interaction with CO_2. The method of synthesis also leads to the presence of a RAFT end-group capable of acting as a polymer-philic anchor group.

This chapter has also identified that copolymers possess improved stabiliser activity compared to PVPi homopolymers, most likely because such polymers optimise the free energy requirements for a CO_2-soluble material, as described by Beckman *et al.*[52] Stabilisers of ~10 kg/mol were typically observed to be of sufficient length to impart steric stabilisation, whilst being of suitably low molecular weight to maintain good CO_2-solubility. Moreover, it has been shown

that adjustment of the composition ratio of the stabiliser results in variations of particle morphology, with micron-sized spherical particles. Whilst these variations are small, it appears there is a compromise between CO_2-solubility and steric stabilising ability, with ~25:75 to 50:50 ratio of PVAc-*s*-PVPi-X stabilisers providing a suitable balance, and allowing optimum polymerisation results to be achieved.

Stabiliser loading also has an impact on the polymerisation, and the copolymer stabilisers were found to operate successfully even at low loading. Increasing the loading was also found to have a significant impact on the final particle size obtained, in agreement with the observations from the literature. [37, 40-43] Whilst alternative co-monomers for polymerisation with VPi were considered, the PVAc-*s*-PVPi-X copolymer still proved the most successful.

These results highlight a route to novel hydrocarbon stabilisers that are inexpensive, highly CO_2-soluble and may be applied very successfully in dispersion polymerisations. Solubility in CO_2 and subsequent stabilisation of the growing polymer particles are crucial factors in dispersion polymerisation, and these hydrocarbon materials are able to provide a solution to both issues by incorporating VPi into the structure. In addition, the RAFT functionality provides a means of anchoring to the PVP particles effectively.

Whilst the stabilisers presented in this section do not currently match the stabilising activity and versatility of fluorinated stabilisers, these PVPi-based materials mark a significant step towards the development of hydrocarbon

alternatives. Future work will exploit these PVPi-based stabilisers, and expand their use in dispersion polymerisation in $scCO_2$ to other monomer systems, and in the development of other surfactant applications.

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Chapter 5: Investigation of Poly(vinyl pivalate) Copolymer Architecture

This chapter focuses on further investigation of the PVPi-based hydrocarbon stabilisers, looking in more detail at changes to the stabiliser architecture. The first section involves the development of block copolymer stabilisers composed of PVAc and PVPi, and the comparison of these structures with statistical copolymer equivalents in terms of both their solubility in the variable volume view cell, and the stabilising ability of these polymers in high pressure polymerisations to produce PNVP particles.

The second part of the chapter begins to consider the effect of stabiliser end-groups; in particular looking at radical-induced reduction for removal of the sulfur moiety and the incorporation of different end-groups *via* variation of the R group in the xanthate employed. Each of these end-group changes were studied to gain a greater understanding of the significance of the xanthate in the final stabiliser structure, and whether this component plays a key role in anchoring to the growing polymer particles in $scCO_2$.

5.1 Introduction

RAFT polymerisation is one of the most successful controlled polymerisation techniques, as it has been applied to a wide range of monomers, is tolerant to a variety of reaction conditions and functional groups, and is relatively simple and inexpensive to implement.[1-4] Throughout this thesis, the method of RAFT polymerisation has been adapted for the synthesis of hydrocarbon stabilisers. The mechanism and key features of RAFT polymerisation are detailed in Chapter 1.

One of the most appealing characteristics of RAFT polymerisation is the ability to access a wide range of architectures using the technique. This controlled radical polymerisation process has been applied in the synthesis of well-defined structures such as gradient, star, block, comb and hyperbranched polymers. In addition to this, the RAFT process enables a range of techniques to be utilised post-polymerisation to manipulate the functionality of the polymer and transform the thiocarbonylthio end-group. In the next section, the application of RAFT polymerisation for the synthesis of block copolymer structures, and the transformation of the incorporated RAFT end-groups of polymers will be considered in more detail.

5.1.1 Block copolymers *via* RAFT Polymerisation

The facile synthesis of block copolymers is one of the key advantages of RAFT polymerisation, resulting in the formation of polymers with thiocarbonylthio end-groups, also known as macro-RAFT agents.[1] This feature gives the resulting polymers the ability to chain extend and form block copolymer architectures.[5]

There are two methods of block copolymer synthesis *via* RAFT polymerisation:[1]

1) Chain extension of the macro-RAFT agent using a second monomer.

2) Attachment of a RAFT agent to a polymer with a functional end-group, allowing the combination of polymers *via* two polymerisation techniques.

Chain extension using a macro-RAFT agent is similar to homopolymerisation *via* the RAFT process. Initially, a macro-RAFT agent is generated from monomer M_1. In the second step, a radical initiator and a second monomer (M_2) are introduced. Polymerisation of monomer M_2 takes place, resulting in formation of the second block, through chain transfer with the macro-RAFT agent synthesised during RAFT polymerisation of the initial monomer, M_1 (Figure 5.1).

The choice of R and Z group of the RAFT agent for block copolymer synthesis is important. The Z group should be chosen to facilitate controlled polymerisation of both monomers. The choice of R group is crucial in that the polymer M_1 generated in the first step needs to act as the leaving group, and so must have comparable or better leaving group ability to polymer M_2, or block copolymerisation will be unsuccessful.[5] In other words, the monomer with a

higher chain transfer rate to the RAFT agent must be polymerised first. This prevents inefficient blocking and allows the achievement of high conversions when chain extension with a second monomer takes place.[5, 6]

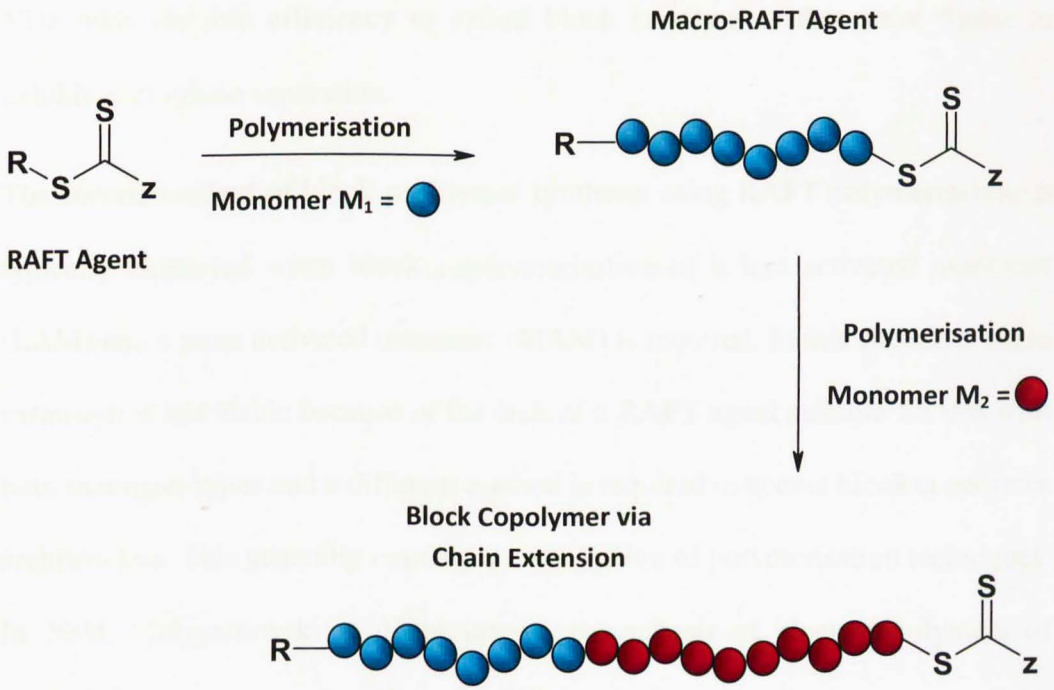


Figure 5.1: Mechanism of block copolymer synthesis *via* method 1. A macro-RAFT agent is formed from monomer M_1, and chain extension of the polymer with monomer M_2 takes place.

Chain extension is the most commonly employed method of block copolymer formation and there have been a number of examples of successful synthesis *via*

the chain extension of a macro-RAFT agent.[6-8] One such example is the successful synthesis of block copolymers of PVAc and PVPi *via* RAFT polymerisation, using a xanthate as the chain transfer agent, demonstrated recently by Lipscomb *et al.*[8] The authors carried out a series of chain extension reactions from xanthate-terminated vinyl ester homopolymers with VAc, VPi, and VBz with variable efficiency to afford block copolymers that were found to exhibit microphase separation.

The second method of block copolymer synthesis using RAFT polymerisation is typically employed when block copolymerisation of a less activated monomer (LAM) and a more activated monomer (MAM) is required. In this situation, chain extension is not viable because of the lack of a RAFT agent suitable for use with both monomer types and a different method is required to access block copolymer architectures. This generally requires a combination of polymerisation techniques. In 2008, Matyjaszewski *et al.* reported the synthesis of block copolymers of PVAc by a successive RAFT and ATRP route.[9] This method afforded block copolymers with a combination of LAMs and MAMs, such as PVAc-*b*-PMMA, which would not have been accessible using chain extension *via* a macro-RAFT agent. Research by groups such as Stenzel *et al.* have also demonstrated the ability to access block copolymers of disparate reactivities through a combination of RAFT and click chemistry.[10] This type of block copolymer synthesis involves the use of click chemistry to circumvent the problems posed by conventional RAFT agents. Homopolymers are synthesised by RAFT polymerisation, and then 'clicked' together without further modification.

Thang *et al.* recently reported an interesting development utilising 'pH switchable' RAFT agents (Figure 5.2).[11]

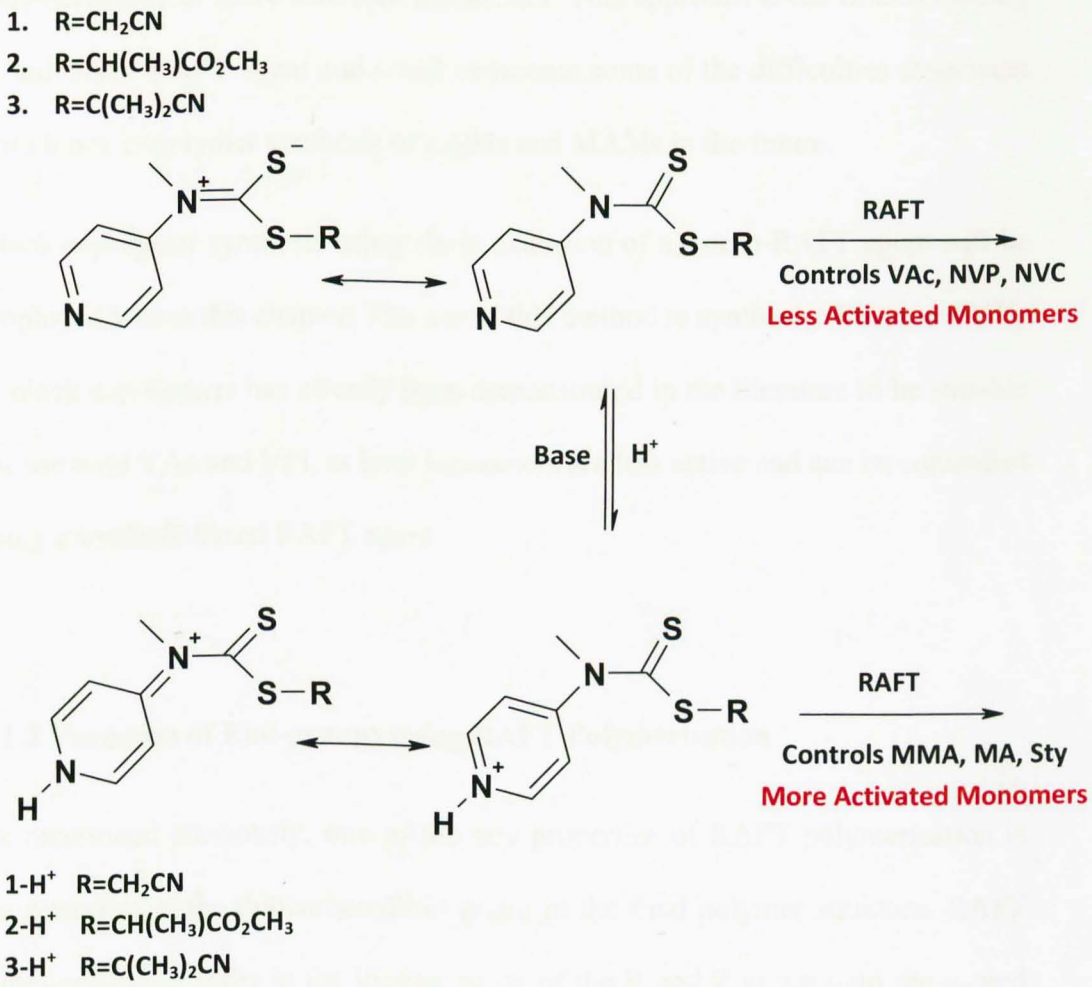


Figure 5.2: Synthesis of block copolymers using a class of switchable RAFT agents, *N*-(4-pyridinyl)-*N*-methyldithiocarbamates, and their pH responsive properties.[11]

A class of switchable RAFT agents, *N*-(4-pyridinyl)-*N*-methyl dithiocarbamates, were used to provide control over the polymerisation of less activated monomers and, after addition of a protic or Lewis acid, became effective in also controlling polymerisation of more activated monomers. This approach is the first to employ a 'universal' RAFT agent and could overcome some of the difficulties associated with block copolymer synthesis of LAMs and MAMs in the future.

Block copolymer synthesis using chain extension of a macro-RAFT agent will be employed within this chapter. The use of this method to synthesise PVAc-*b*-PVPi-X block copolymers has already been demonstrated in the literature to be suitable for use with VAc and VPi, as both monomers are less active and can be controlled using a xanthate-based RAFT agent.

5.1.2 Variation of End-groups using RAFT Polymerisation

As mentioned previously, one of the key properties of RAFT polymerisation is the retention of the thiocarbonylthio group in the final polymer structure. RAFT polymerisation results in the incorporation of the R and Z group onto the α- and ω-end of the polymer respectively. This end-group retention can provide a means of functionalising the polymer through the selection of appropriate R and Z groups of the initial RAFT agent. The R group in particular can be utilised to introduce specific functionality to the α-end of the polymer with little difficulty. This method is an efficient way of introducing terminal functionality by simply

tailoring the RAFT agent for the purpose, and examples of this have been reported in the literature.[12-17]

In addition to functionalisation at the α-end of the polymer through the employment of tailored RAFT agents, modifications to the thiocarbonylthio end-group at the ω-end are often desired. A range of processes for end-group transformation have been developed, and are highlighted in Figure 5.3.[1, 18, 19]

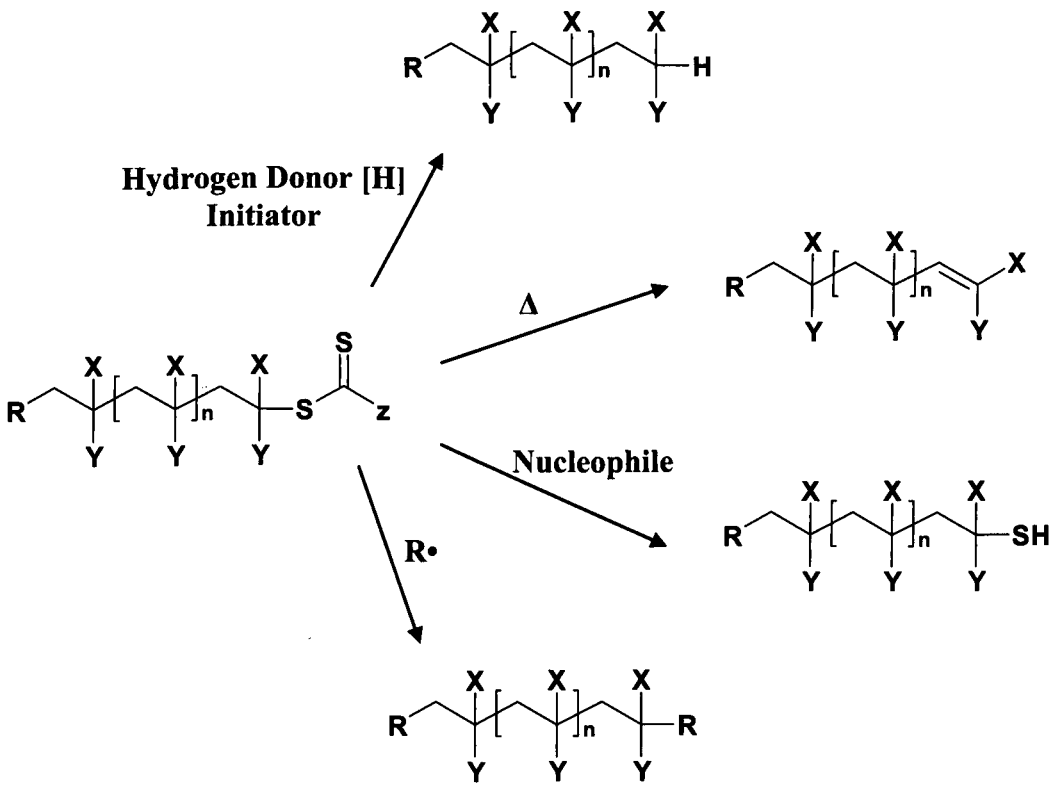


Figure 5.3: Summary of some of the key methods of thiocarbonylthio end-group modification post- RAFT polymerisation. From top to bottom: a) Radical-induced reduction; b) Thermolysis; c) Reaction with nucleophiles; d) Addition-fragmentation coupling.

Thiocarbonylthio groups of a RAFT-terminated polymer will undergo reaction with nucleophiles such as amines[20-22] and hydroxides,[23, 24] and also with ionic reducing agents such as boron hydrides.[20, 25, 26] These transformations lead to the production of a polymer with a thiol end-group (Figure 5.4). Problems associated with this type of reaction involve the formation of polymeric disulfides of twice the molecular weight of the original polymer. However, cleaner methods of thiol end-group generation can also be employed, using reducing agents such as sodium bisulfite, which are employed to supress such side reactions.[22, 27] It is also important to note that the resulting -SH end-group is sensitive to oxidation.

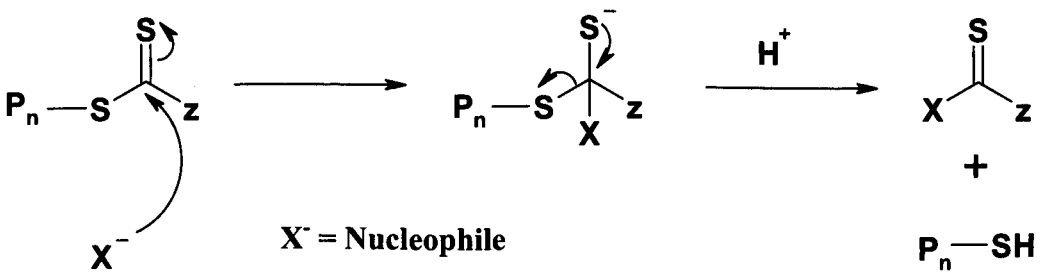


Figure 5.4: Production of thiol end-group *via* reaction of RAFT-terminated polymer with nucleophiles *e.g* aminolysis.[19]

Thiol-terminated polymers can be used in a number of applications, and also as precursors to other polymer end-group functionalities and architectures. Thiol-ene processes have been extensively employed to trap the thiol by the addition of an activated alkene (Michael acceptor).[28-31] The thiol end-group can also be

employed in thiol-ene reactions to introduce specific functionalities into the polymer such as fluorescently labelled groups for drug delivery applications.[32] Thiol-terminated polymers can also be biofunctionalised through conjugation of biomolecules to the polymer which can often lead to improved stability and pharmokinetics, and demonstrates the potential of RAFT synthesised polymers in biological applications.[33-36] Oxidative coupling of polymers with thiol end-groups can also be utilised to produce multiblock copolymers.[37-39]

Complete desulfurisation of the thiocarbonylthio-terminated polymer can also be obtained *via* thermolysis.[40-42] The process involves thermal elimination, requiring no additional reagents and resulting in the production of a polymer with an unsaturated chain end. However, the process also requires that any functionality within the polymer must be stable to the thermolysis conditions, in particular high temperatures (~120 to 200 °C) or degradation of the polymer can occur. The technique has been used for a wide range of polymers, including the thermolysis of xanthate-terminated polymers. The mechanism of end-group loss has been found to be dependent upon both the type of polymer and the RAFT end-group.[19] Whilst thermolysis of *S*-polystyrene *O*-isobutyl xanthate at 180 °C resulted in selective elimination to provide 2-butene and the production of a polymer with a thiol end-group is observed,[43] a similar study using *S*-poly(vinyl acetate) *O*-ethyl xanthate suggests a different mechanism involving initial C–S bond homolysis triggering degradation, followed by backbiting and β-scission to form a macromonomer with an exo-methylene double bond (Figure 5.5).[44]

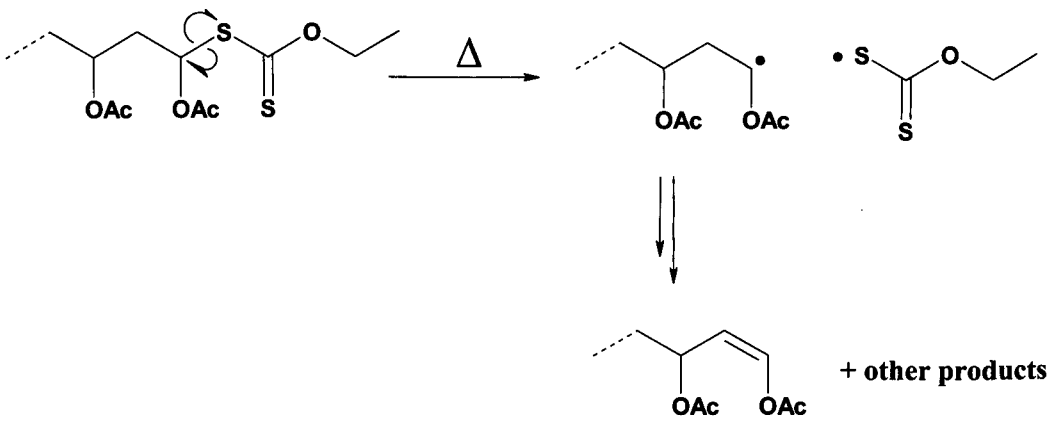


Figure 5.5: Mechanism of thermolysis of *S*-poly(vinyl acetate) *O*-ethyl xanthate.

Radical-induced end-group removal involves the use of free radicals to modify the ω-end of the RAFT-terminated polymer, using a radical species to add to the reactive C=S bond and forming an intermediate radical, which can fragment or react with a trapping group and terminate.[1] Addition-fragmentation coupling employs an excess of initiator and high temperatures to promote loss of the RAFT agent through radical-induced ester exchange. This has been demonstrated by groups such as Perrier *et al.* in the removal of the dithiobenzoate end-group using AIBN in a 20-fold excess.[12] The RAFT equilibrium is displaced towards the formation of the polymeric chain radical, irreversibly combining with the excess AIBN radicals, leading to a polymer terminated with a cyano isopropyl group.

This mechanism can also be adapted using a hydrogen atom donor source, leading to radical-induced reduction, and the conversion of the thiocarbonylthio end-

group to a H-atom. Radical-induced reduction is based upon the Barton-McCombie reaction for deoxygenation of secondary alcohols, in which the xanthate O-alkyl is a good homolytic leaving group (Figure 5.6).[45-48] This method is well known for the reduction of low molecular weight thiocarbonylthio compounds.

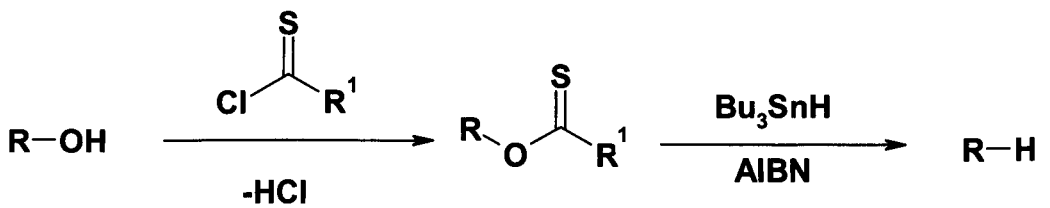


Figure 5.6: Barton-McCombie reaction for the deoxygenation of secondary alcohols.

An effective hydrogen donor transfer agent is required for a successful reduction. Stannanes are some of the most efficient hydrogen atom donors available, and compounds such as tributylstannane have previously been used with success, but with such donors there are issues with toxicity and by-product removal.[42] Tris(trimethylsilyl)silane has also been considered as an alternative hydrogen donor atom source but a reduced efficiency and bimolecular terminations were observed.[42] Hypophosphate salts such as *N*-ethylpiperidine hypophosphite (EPHP) have recently attracted attention as alternatives to tin hydrides, being much less toxic and also being water soluble, allowing for a simple work-up after reaction (Figure 5.7).

Recently, Thang *et al.* demonstrated the application of EPHP in the synthesis of H-terminated polymers through the reduction of the RAFT end-group.[49] The mechanism of radical-induced reduction using EPHP is described in section 5.3.2.2 of this chapter.

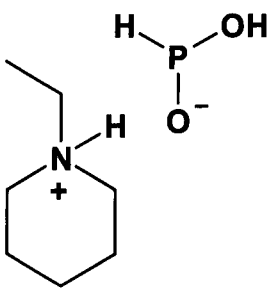


Figure 5.7: The structure of the hypophosphate salt, EPHP.

This introductory section highlights that RAFT polymerisation allows a variety of architectures and end-group functionalities to be accessed through a number of simple and effective processes. The aim of this chapter is to investigate the application of some of these techniques, first considering the effect of block copolymer architectures in comparison to statistical copolymers as stabilisers, and also looking at the impact of a few typical end group transformations on the solubility and stabilising ability of polymers in $scCO_2$.

5.2 Experimental

5.2.1 Materials

2-bromopropionic acid (99 %) was obtained from Alfa Aesar and sodium carbonate (99 %) was supplied by Fischer Scientific. *N*-ethylpiperidine hypophosphite (EPHP) (95 %) and sodium hydroxide (99 %), and monomers vinyl acetate (VAc) (99 %) and vinyl pivalate (VPi) (99 %) were purchased from Sigma Aldrich. *N*-vinyl pyrrolidone (NVP) (97 %, 0.001% *N,N'*-di-*sec*-butyl-p-phenylenediamine inhibitor) was obtained from Fluka. All monomers were stored at 3-4 °C and purified prior to use by passing through a column of activated aluminium oxide, and subsequently degassing *via* three freeze-pump-thaw cycles. The initiator 2, 2'-azobis(isobutyronitrile) (AIBN) was obtained from Acros and purified by recrystallisation twice from cold methanol. Initiator 2,2'-azobis (4-methoxy-2,4-dimethylvaleronitrile) (V-70) (WAKO, 95 %) was used as received. Dry CO_2 (99.99 %) and nitrogen (99.99 %) were purchased from BOC.

5.2.2 Synthesis and Polymerisations

5.2.2.1 Xanthate X2 Synthesis

An additional RAFT/MADIX agent with a –COOH R group was employed in this chapter to investigate the effect of incorporating different end-group functionality in the stabiliser architecture. The synthesis of xanthate X2 *propanoic acid O-ethyl xanthate* employed in this chapter is adopted from the literature.[50, 51]

Synthesis of Xanthate X2: Potassium O-ethyl xanthate (15.12 g, 9.37×10^{-2} mol) was dissolved in distilled water (45 mL). 3.3 M NaOH (22 mL) was added while stirring. The mixture was then cooled in an ice bath and 2-bromopropionic acid (11.4 g, 7.5×10^{-2} mol) was added dropwise to the reaction mixture. The reaction was left to proceed for 16 h at room temperature. The pH of the solution (pH = 7 at the end of the reaction) was adjusted with 2 M HCl to pH = 1. The product was initially extracted with diethyl ether (2 × 200 mL) and then extracted from the ethereal phase with aqueous sodium carbonate (25 g in 250 mL water, 2 × 50 mL). The pH was readjusted to pH = 3 with 1 M HCl. The product was extracted with diethyl ether (200 mL), the ethereal phase dried over anhydrous magnesium sulfate and the solvent evaporated under reduced pressure. A pale yellow solid crystallised during evaporation. The product was recrystallised from hexane and dried overnight in the vacuum. Yield: 61%. ^{1}H NMR ($CDCl_3$): δ = 11.14, (br, s, 1H), 4.67 (2×q, 2H, b), 4.44 (q, 1H, c), 1.63 (d, 3H, d), 1.44 (t, 3H, a).

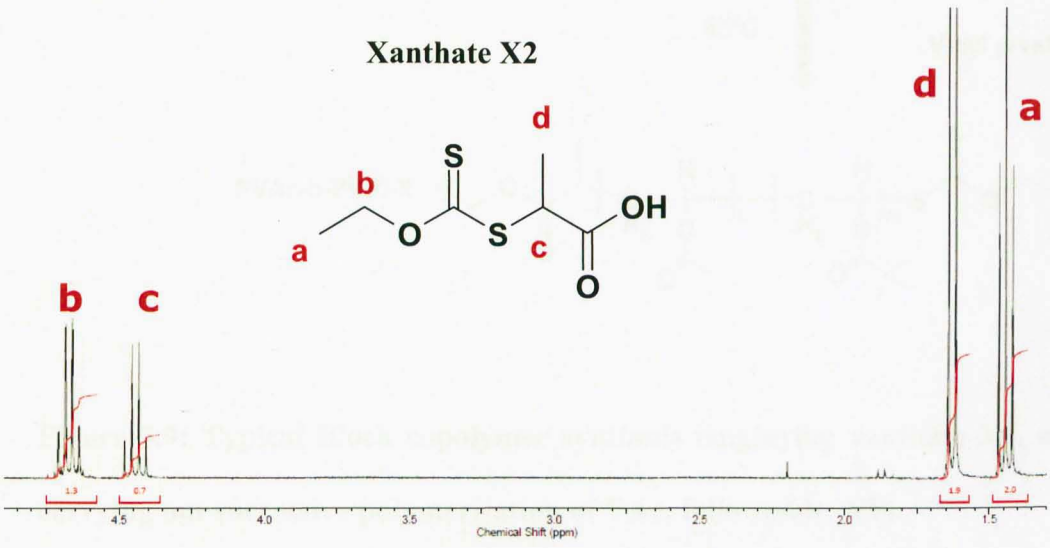


Figure 5.8: ^{1}H NMR of propionic acid O-ethyl xanthate (X2).

5.2.2.2 Block Copolymer Synthesis

Block copolymer synthesis was carried out by first producing one homopolymer chain (*e.g* **PVAc-X**) *via* the xanthate X1. This was then employed in a second polymerisation reaction in which the homopolymer acted as the RAFT/MADIX agent, as the xanthate end-groups were incorporated in the final polymer produced in the first step and able to reinitiate RAFT polymerisation. A schematic of a typical block copolymer synthesis is shown (Figure 5.9).

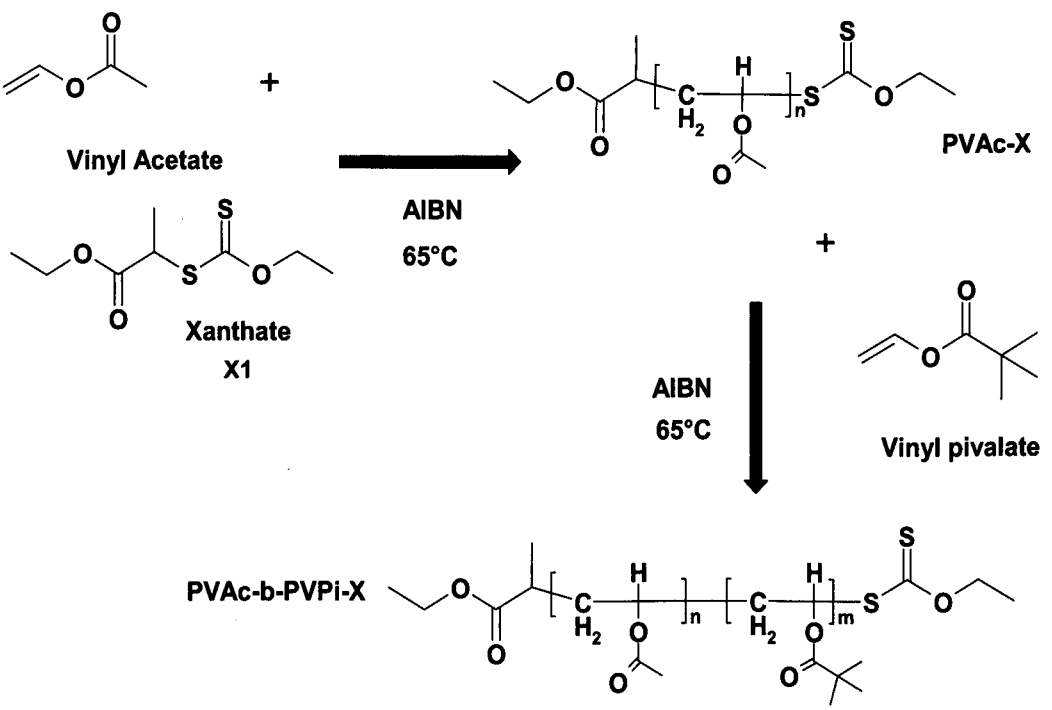


Figure 5.9: Typical Block copolymer synthesis employing xanthate X1, and carrying out successive polymerisation of VAc, followed by VPi.

Typical Block copolymer synthesis: Vinyl pivalate (5.00 g, 3.9 x 10^{-2} mol), AIBN (0.02 g, 1.0 x 10^{-4} mol) and xanthate X1 (0.23 g, 1.0 x 10^{-3} mol) were added to a 50 mL round bottomed flask equipped with stirrer bar and three-way stop cock. The flask contents were subjected to three freeze-pump-thaw cycles on the Schlenk line and charged with an inert gas. The reaction flask was immersed in an oil bath at 65 °C for 24 h. The polymer product was purified *via* precipitation into a mixture of ice cold methanol: water (4:1). The final product was filtered and dried in the oven. M_n: 4.5 kg/mol, PDI: 1.24, Conversion: 63%.

In the second stage, VAc (5.00 g, 5.8 x 10^{-2} mol), poly(vinyl pivalate) macro-xanthate polymer (3.74 g, 8.3 x 10^{-4} mol), AIBN (0.014 g, 8.3 x 10^{-5} mol) and dry toluene (5 mL) were added to a 50 mL round bottomed flask with stirrer bar and three-way stop cock. The flask was degassed using three freeze-pump-thaw cycles. The flask was immersed in an oil bath at 65 °C for 24 h. The product was precipitated into a mixture of ice cold methanol: water and vacuum dried overnight. M_n: 10.2 kg/mol, PDI: 1.45, Ratio: 51:49, Conversion: 75% (Table 5.1, entry 8).

5.2.2.3 Radical-induced Reduction

Radical-induced reduction allows the thiocarbonylthio group of RAFT-synthesised polymers to be replaced with a hydrogen atom. The process involves thiocarbonylthio compounds undergoing facile reaction with radicals by addition–fragmentation. In this chapter, both X1 and X2-terminated polymers were reduced

using *N*-ethylpiperidine hypophosphite (EPHP).[49] EPHP was employed in a 20-fold excess w.r.t polymer, and 0.5 equivalents of AIBN were used, resulting in [Polymer]:[EPHP]:[I] of 1:20:0.5.

Typical Radical-induced Reduction: PVAc-*s*-PVPi-X polymer (9400 g/mol, 2.50 g, 2.66×10^{-4} mol), *N*-ethylpiperidine hypophosphite (0.95 g, 5.32×10^{-3} mol) and AIBN (0.02 g, 1.33×10^{-4} mol) were dissolved in toluene (5 mL) in a sealed 50 mL round-bottomed flask. The vessel was subjected to three freeze-pump-thaw cycles and backfilled with nitrogen. The reaction flask was heated at 80 °C for ~6 h. After reaction completion, a distinct colour change from a clear solution to deep yellow was observed, indicating the presence of sulfur by-products. The reaction was quenched and cooled in an ice bath. The solution was washed with water (3 × 50 mL) and the toluene removed under reduced pressure. The polymer product was dissolved in THF, precipitated into a mixture of ice cold methanol: water (4:1) and vacuum dried overnight.

5.3 Results and Discussion

5.3.1 Block Copolymer Architectures

In Chapters 3 and 4, both the solubility and the stabilising ability of statistical copolymers of VAc and VPi were studied in detail. Often, the polymer architecture can be a significant factor in the ability of a polymer to act as a stabiliser material. In order to understand this relationship further, statistical and block copolymers were targeted for comparison.

5.3.1.1 Block Copolymer Synthesis

A series of block copolymers of VAc and VPi were synthesised and both the solubility and stabilising ability of these materials was determined in order to compare the effectiveness of the two types of stabiliser architecture. Further to this, a range of block copolymers of varying molecular weight and comparable composition were produced. The results of the block copolymerisations are shown in Table 5.1.

Both block and statistical copolymers exhibited narrow PDI of 1.31-1.54 and molecular weights close to those targeted. In the case of the block copolymers, molecular weights were slightly higher than theoretical value in the majority of cases. High conversions were also obtained and experimental ratios were close to those of the feed ratios for the most part.

Table 5.1: Block Copolymer Stabilisers of Varying Ratio and Molecular Weight.

Entry	Polymer	M:R:I[a]	Block A (M_n, PDI)[a]	$M_{n,th}$ (Kg/mol)	$M_{n,expt}$ (Kg/mol)[a]	PDI[a]	Feed Ratio	Expt. Ratio[b]	Conv. (%)[b]	T_g (°C)[c]
1		109:1:0.1	-	11.6	12.1	1.46	25:75	24:76	89	40.7
2	**PVAc-*s*-PVPi-X**	124:1:0.1	-	11.1	11.6	1.40	60:40	51:49	85	50.2
3		140:1:0.1	-	12.7	11.7	1.38	80:20	74:26	94	61.7
4		69:1:0.1	2.2K, 1.20	9.1	12.3	1.54	25:75	27:73	83	36.2, 70.3
5		53:1:0.1	4.2K, 1.27	8.3	11.9	1.45	50:50	46:54	75	39.8, 66.1
6	**PVAc-*b*-PVPi-X**	33:1:0.1	7.7K, 1.33	9.8	11.8	1.52	75:25	70:30	82	41.6, 67.5
7		25:1:0.1	2.2K, 1.20	4.8	6.7	1.31	50:50	46:54	79	37.0, 53.4
8		47:1:0.1	4.5K, 1.24	7.9	10.2	1.45	50:50	51:49	75	39.3, 64.1
9		78:1:0.1	7.0K, 1.25	12.6	15.8	1.52	50:50	47:53	74	41.0, 72.5

Polymerisation conditions: Statistical copolymers synthesised *via* bulk polymerisation at 65 °C for ~4 h, and block copolymers synthesised *via* solution polymerisation in dry toluene (5 mL) at 65 °C for 24 h. [a]Experimental M_n and PDI obtained from GPC-RI detector using THF eluent and PS standards. [b]Conversion and PVAc:PVPi ratio determined from ^{1}H NMR in $CDCl_3$. Ratios correspond to PVAc:PVPi composition. [c]T_g obtained from DSC analysis.

Glass transition temperatures were also as expected. In the case of the block copolymer structures, two T_g values were obtained, in comparison to the single T_g characteristic of a PVAc-*s*-PVPi-X statistical copolymer (Table 5.1; entries 4-11). This is evidence of block copolymer formation. Whilst the statistical copolymers possess a T_g which varies smoothly with composition between the T_g values of the two homopolymers, the block copolymers exhibit two T_g values (Figure 5.10).

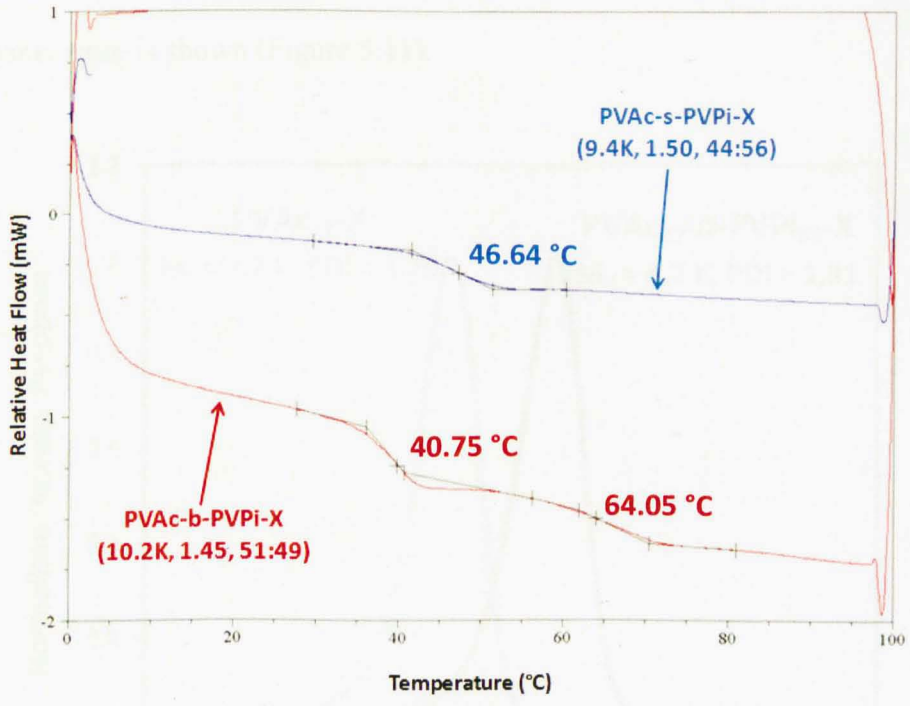


Figure 5.10: Comparison of T_g for a typical set of statistical and block copolymer equivalents with 50:50 ratio (Table 5.1, entries 1 and 8 respectively).

These are close to the values for the component homopolymers; the first T_g corresponding to the PVAc block, and a higher T_g for the PVPi block within the structure. As the two types of monomer unit exist as distinct and separate blocks within the structures, the T_g values are also much more defined and therefore a value is observed for each monomer. The observation of two T_g's is evidence of segregation of different types of units into different regions of the material, and suggests a block copolymer structure.[52]

The GPC traces of the block copolymers can also be considered. A typical block copolymer trace is shown (Figure 5.11).

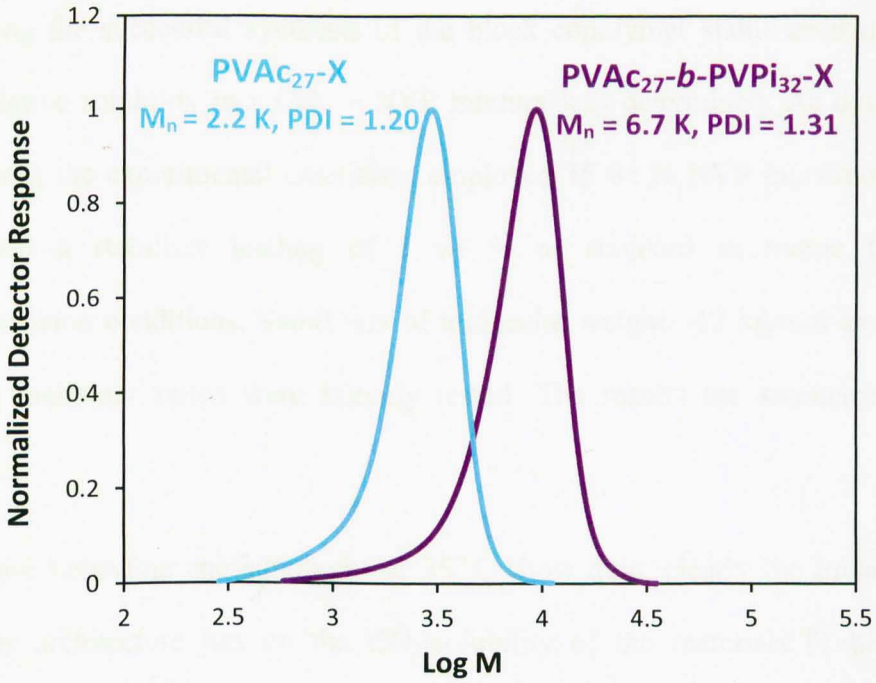


Figure 5.11: Characteristic block copolymer GPC trace, showing initial PVAc-X block, followed by chain extension to yield PVAc-*b*-PVPi-X block copolymer structure. GPC trace obtained using data from Table 5.1; entry 7.

The initial PVAc-X starting block of 27 VAc units is extended by 32 units of VPi upon block copolymerisation. This distinct shift to higher molecular weight is evidence of chain end growth and indicates block copolymer formation is taking place. There is also no distinct peak corresponding to a PVAc-X homopolymer signal within the block copolymer sample trace, confirming there is no significant residual homopolymer present in the sample, which would affect both solubility and stabilising ability using the material.

5.3.1.2 Phase Behaviour of Block Copolymers in scCO$_2$

Following the successful synthesis of the block copolymer stabiliser materials, their relative solubility in a CO_2 + NVP mixture was determined. As described previously, the experimental conditions employed 15 wt % NVP monomer w.r.t CO_2, and a stabiliser loading of 5 wt % as standard to mimic typical polymerisation conditions. Stabilisers of molecular weight ~12 kg/mol and with varying monomer ratios were initially tested. The results are summarised in Table 5.2.

The phase behaviour measurements at 35 °C show quite clearly the impact the stabiliser architecture has on the CO_2-solubility of the materials (Table 5.2, column 7). The phase behaviour of the blocks was determined, and as with the statistical copolymers, an improvement in solubility is observed as the proportion of PVPi is increased within the sample. This follows the same trend exhibited by the statistical copolymers in Chapter 3 when comparing PVAc: PVPi ratio.

Table 5.2: Solubility of Key Block and Statistical Copolymers in $scCO_2$.

Entry	Polymer	$M_{n,expt}$ (Kg/mol)[a]	PDI[a]	Ratio (PVAc:PVPi)[b]	DP[c]	Cloud Point (bar)[d]
1		12.1	1.46	24:76	101	153.9
2	**PVAc-*s*-PVPi-X**	11.6	1.40	51:49	107	170.1
3		11.7	1.38	74:26	118	194.4
4		12.3	1.54	27:73	102	171.2
5	**PVAc-*b*-PVPi-X**	11.9	1.45	46:54	106	182.8
6		11.8	1.52	70:30	134	214.9

[a]Experimental M_n and PDI obtained from GPC-RI detector using THF eluent and PS standards. [b]Ratio determined from ^1H NMR in $CDCl_3$. [c]Degree of polymerisation calculated using M_n and ratio. [d]Cloud point at 35 °C determined using variable volume view cell.

However, upon comparison of the block copolymer with the equivalent statistical copolymer of a similar ratio, it can be seen that the statistical copolymers are more soluble (Figure 5.12). The PVAc-*b*-PVPi-X block copolymer shows slightly reduced affinity for CO_2, and for all block copolymers of varying composition at ~12 kg/mol, there is ~10 to 20 bar increase in the cloud point values. This is also expected to some extent, as the more soluble PVPi component is concentrated at one end of the chain in the block copolymers, rather than statistically arranged throughout the structure. This segregation of the two monomer types will result in decreased solubility overall, as only the PVPi portion of the block will have improved CO_2-solubility, whilst in the case of the statistical copolymer, the VPi units are statistically interspersed throughout the structure and will aid dissolution of the whole polymer chain.

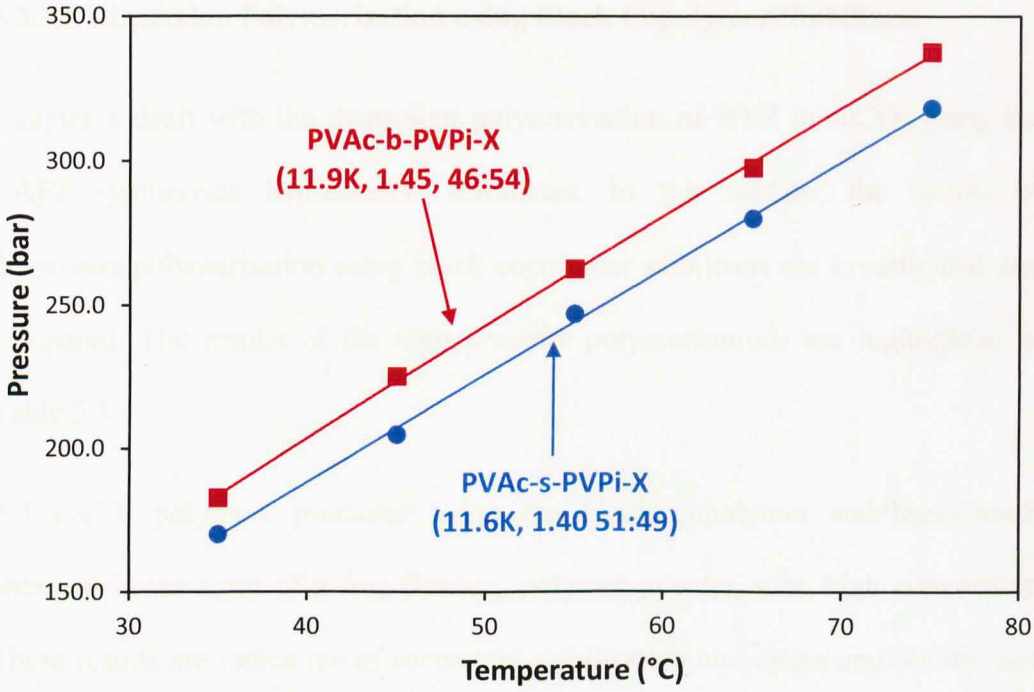


Figure 5.12: Phase behaviour curve of PVPi-based copolymers of comparable molecular weight and composition, with different stabiliser architectures (Table 5.2, entries 2 and 5). Statistical copolymer structure exhibits lowest cloud point values, and therefore is the most CO_2-soluble architecture.

5.3.1.3 Dispersion Polymerisation using Block Copolymer Stabilisers

Chapter 4 dealt with the dispersion polymerisation of NVP in $scCO_2$ using the RAFT synthesised hydrocarbon stabilisers. In this section, the results of dispersion polymerisation using block copolymer stabilisers are investigated and compared. The results of the high pressure polymerisations are highlighted in Table 5.3.

All PNVP polymers produced using the block copolymer stabilisers were obtained in the form of a free-flowing, polymer powder, with high conversion. These results are indicative of successful stabilisation and dispersing ability, and comparable to PNVP products obtained using a statistical copolymer stabiliser. Comparable molecular weights and PDI values were also obtained using both types of stabiliser architecture (Table 5.3, column 5 and 6).

However, whilst stabilisation using the block copolymers was successful, it is clear that the block copolymer architecture is less effective in dispersion polymerisation of NVP when compared to a statistical copolymer. It was observed that the resulting particle size diameter was larger using a block copolymer stabiliser compared to the statistical copolymer equivalent of similar ratio and molecular weight. A broader range of particle sizes was also observed, highlighted by the increased C_v value obtained for all of the block copolymer stabilisers (Table 5.3, column 8).

Table 5.3: PNVP Polymerisations in $scCO_2$ using Block Copolymer Stabilisers.

Stabiliser Details				PNVP Product					
Entry	Polymer	M_n, PDI, Ratio[a]	Cloud Point (bar)[b]	M_w (kg/mol)[c]	PDI[c]	D_n (μm)[d]	C_V (%)[e]	Yield (%)[f]	Morphology
1		12.1K, 1.46, 24:76	153.9	223	4.3	2.4	25.2	89	Powder
2	**PVAc-*s*-PVPi-X**	11.6K, 1.40, 51:49	170.1	231	5.3	2.1	23.0	83	Powder
3		11.7K, 1.38, 74:26	194.4	259	5.9	1.9	20.7	84	Powder
4		12.3K, 1.54, 27:73	171.2	260	5.3	3.5	40.7	74	Powder
5		11.9K, 1.45, 46:54	182.8	261	5.2	3.2	41.2	82	Powder
6		11.8K, 1.52, 70:30	214.9	223	4.8	3.5	41.0	89	Powder
7	**PVAc-*b*-PVPi-X**	6.7K, 1.31, 46:54	126.9	325	5.8	-	-	91	Powder
8		10.2K, 1.45, 51:49	158.2	250	6.5	2.8	38.9	92	Powder
9		15.7K, 1.52, 47:53	207.2	306	6.1	7.4	29.0	97	Powder

Polymerisation conditions: $scCO_2$ polymerisation at 35 °C for 48 hours with V-70 initiator and 5 wt % of stabiliser. [a]Stabiliser M_n and PDI determined *via* GPC-RI with THF eluent and PS standards, Ratio determined from ^1H NMR. [b]Stabiliser cloud point determined using variable volume view cell. [c]Experimental M_w and PDI obtained from GPC-RI detector in chloroform with 5 % triethylamine using PS standards. [d]Mean particle diameter as determined from sampling of ~100 particles of a typical SEM image. [e]Coefficient of variance as determined by equation $C_v = (\sigma/D_n) \times 100$. [f]Yield determined gravimetrically.

Comparison of Block and Statistical Copolymer Stabilisers

The extent of the differences in particle morphology and size distribution using the two stabiliser types can be observed in the corresponding SEM micrographs (Figure 5.13).

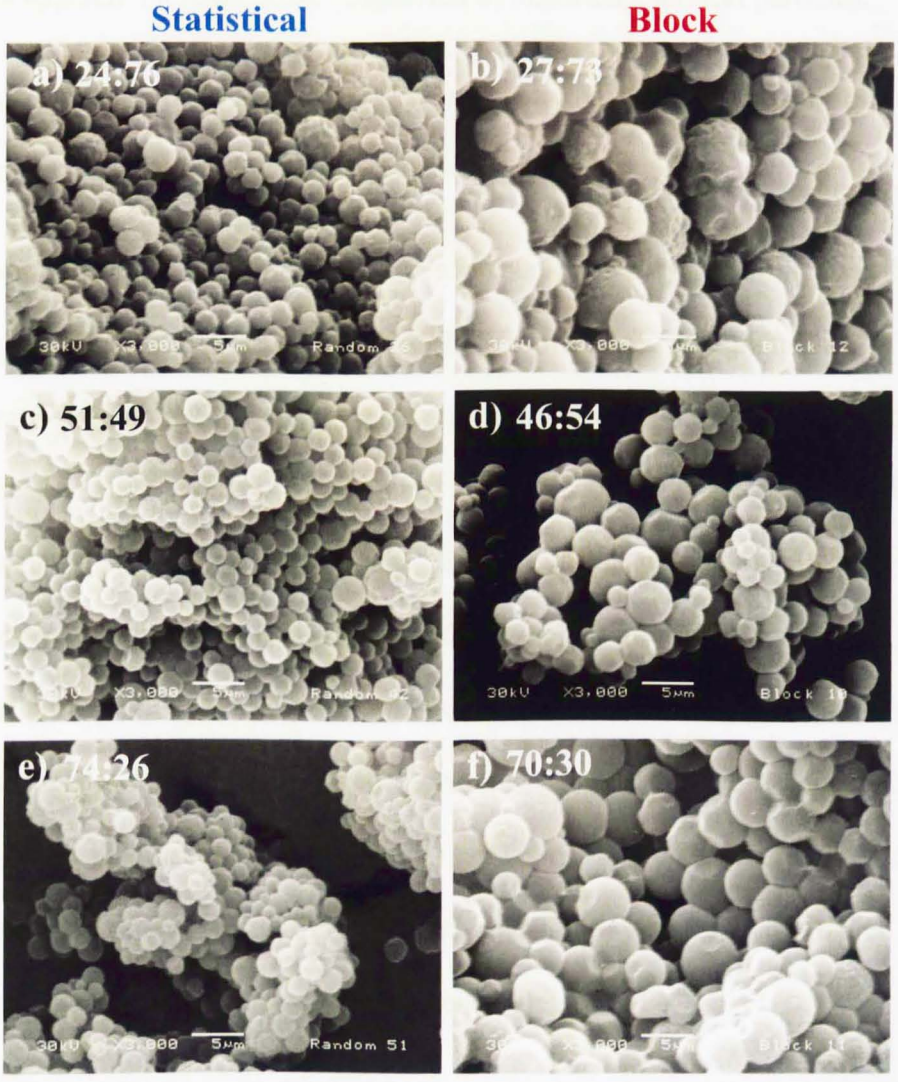


Figure 5.13: Comparison of PNVP products using block and statistical copolymer stabilisers of ~12 kg/mol and varying composition. (a) PVAc-*s*-PVPi-X 24:76; (b) PVAc-*b*-PVPi-X 27:73; (c) PVAc-*s*-PVPi-X 51:49; (d) PVAc-*b*-PVPi-X 46:54; (e) PVAc-*s*-PVPi-X 74:26; (f) PVAc-*b*-PVPi-X 70:30.

Whilst the difference in size between block and statistical copolymer equivalents is evident, there is also a clear difference in the shape of the PNVP particles. All of the stabilisers allow for spherical particle formation, but when employing block copolymer stabilisers, the surface of the resulting particles is less well-defined, with an apparent increase of the proportion of distorted spherical particles.

The size distribution effects can also be illustrated more clearly by plotting a histogram of particle size diameter (Figure 5.14).

The histograms give a clear graphical representation of the probability distribution of the particle size diameter (D_n) of the PNVP product. The comparison of these two graphs highlights the conclusions drawn when considering the SEM images and the D_n and C_v data. Whilst the statistical copolymers result in PNVP microspheres with a relatively tight distribution of particle sizes, the block copolymer stabilisers exhibit less control over the morphology, and a much broader particle size distribution is produced. As a result, the mean particle size diameter is also larger for the block copolymer sample. Although only the 50:50 PVAc:PVPi stabiliser composition is shown, 25:75 and 75:25 PVAc:PVPi compositions were observed to follow a similar trend, with a much broader range of particle sizes for the block copolymer equivalents.

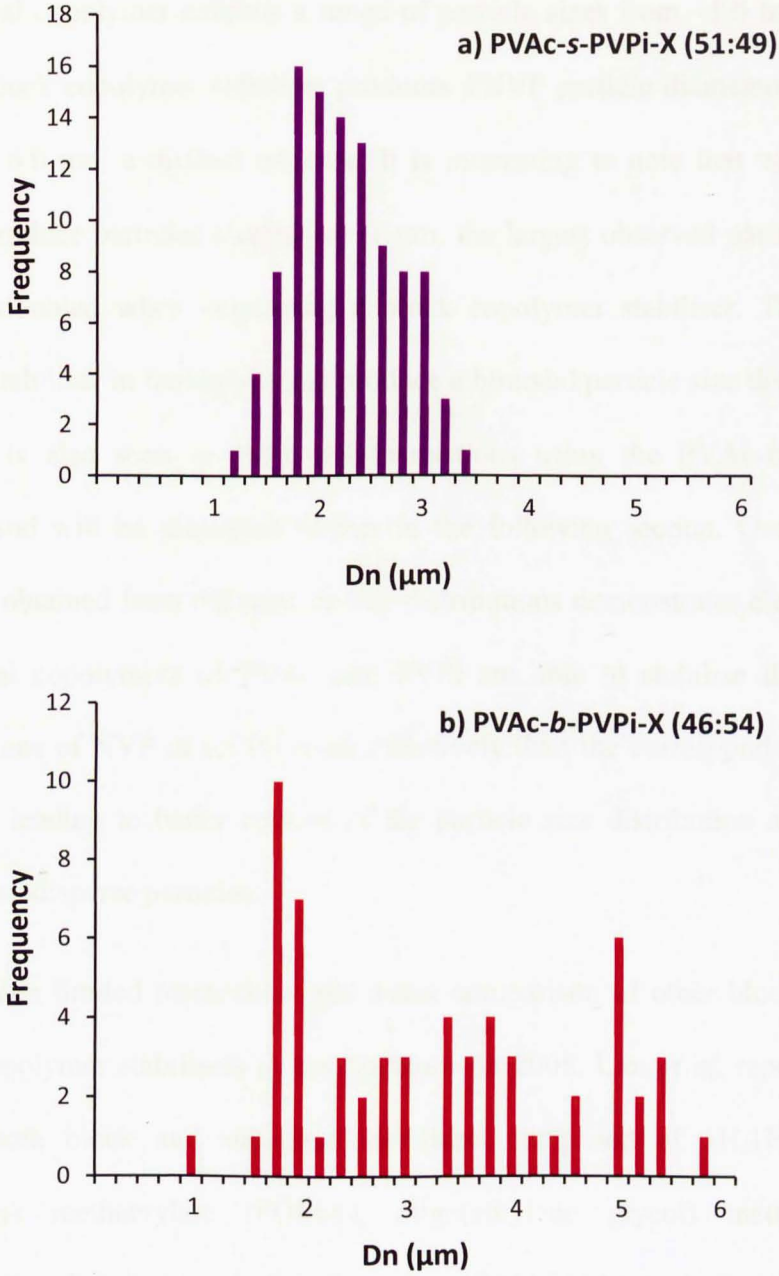


Figure 5.14: Histogram of particle diameters for block and statistical copolymers of comparable molecular weight (~12.0 K) and 50:50 PVAc:PVPi composition, comparing ~100 particles from SEM images. Results obtained from data in Table 5.3, entries 2 and 5.

The statistical copolymer exhibits a range of particle sizes from ~1.0 to 3.5 μm, whilst the block copolymer stabiliser produces PNVP particle diameters ranging from 1.0 to 6.0 μm; a distinct increase. It is interesting to note that while both stabilisers produce particles starting at ~1 μm, the largest observed particle sizes are almost doubled when employing a block copolymer stabiliser. The block copolymer stabiliser in fact appears to produce a bimodal particle size distribution. This effect is also seen in other polymerisations using the PVAc-*b*-PVPi-X stabilisers, and will be discussed further in the following section. Overall, the information obtained from the particle size distributions demonstrates clearly that the statistical copolymers of PVAc and PVPi are able to stabilise dispersion polymerisations of NVP in $scCO_2$ more effectively than the corresponding block copolymers, leading to better control of the particle size distribution and more uniform, monodisperse particles.

There has been limited research on the direct comparison of other block versus statistical copolymer stabilisers in the literature. In 2008, Lim *et al.* reported the design of both block and statistical stabilisers composed of 1H,1H,2H,2H-perfluorooctyl methacrylate (FOMA), oligo(ethylene glycol) methacrylate (OEGMA), dimethyl amino ethyl methacrylate (DMAEMA), and ethylene oxide (EO).[53] These polymers were employed in the dispersion polymerisation of 2-hydroxyethyl methacrylate (HEMA) in $scCO_2$. In all cases, dispersion was successful and a free-flowing powder obtained. It was noted that while the statistical copolymers produced micron-sized particles, the block copolymeric stabilisers resulted in the formation of particles <500 nm in diameter. The authors

suggested that the block copolymers could be adsorbing more strongly, leading to the difference in particle size obtained using the two different architectures.

Shiho *et al.* reported the application of statistical copolymer stabilisers poly(FOMA)-*s*-(Sty) and poly(FOMA)-*s*-(SiMA) in the dispersion polymerisation of styrene in $scCO_2$.[54] The statistical copolymer stabilisers were found to function effectively, allowing for the successful dispersion polymerisation of styrene, generating micron-sized PS colloids. The authors noted this was in contrast to the submicron particles obtained using block copolymers of PFOA and PS as a stabiliser.

Comparisons have also been made in conventional organic solvents. Holder *et al.* reported the synthesis of three statistical and three block copolymers of MMA and octadecyl acrylate (ODA) by ATRP.[55] These copolymers were assessed for their application as stabilisers in the one step non-aqueous dispersion polymerisation of MMA in a non-polar solvent mixture of hexane and dodecane. In all cases stable spherical micro-particle colloidal dispersions were formed with particle diameters in the range of 0.4 to 2.7 μm. The statistical copolymers were synthesised for direct comparison with the assumption that they would not be effective. However, both types of stabiliser functioned successfully. This surprising observation was attributed to the synthesis of the stabilisers in which the reactivity ratios of the monomers were sufficiently different that compositional drift occured during the polymerisation, leading to gradient copolymers with very long segments of ODA sufficient for steric stabilisation.

To summarise, the study of block *vs.* statistical copolymers in the dispersion polymerisation of NVP in $scCO_2$ has shown that the statistical copolymers act as more efficient stabilisers, and produce smaller particles than the block copolymer equivalents. This is in contrast to the findings from the literature, which generally show block copolymers give smaller particle size diameters, and often tend to function more effectively than statistical copolymers. However, it is difficult to compare the stabilising ability of other block copolymer stabilisers with the PVAc-*b*-PVPi-X block copolymer stabilisers described in this thesis. Typically, block copolymer stabilisers employed in other studies utilise one of the blocks as the anchor group.

However, in this work, it is assumed that it is the RAFT agent that provides the anchor portion, and this is the same in each case, whether block or statistical. Therefore, both PVAc and PVPi blocks are likely to contribute to the CO_2-philic component of the surfactant, and a statistical copolymer arrangement will simply provide better solubility for the CO_2-philic portion of the statistical copolymer stabiliser. This will result in improved overall effectiveness of the statistical copolymer stabilisers compared to the block copolymer stabilisers.

Variation of Block Copolymer Molecular Weight

Next, block copolymers of varying molecular weight were synthesised in order to determine whether the chain length of the block copolymer stabilisers has any impact on the PNVP products of dispersion polymerisation in $scCO_2$.

As shown in Table 5.3, block copolymer stabilisers of different molecular weights and a composition of ~50:50 PVAc:PVPi were produced. The solubility of these materials was as expected, and reduced solubility and higher cloud point pressures are observed as the molecular weight, and the chain length, of the stabiliser is increased (Table 5.3, entries 5, 7, 8, 9). This follows the same trend as observed in Chapter 3, in which the PVAc-*s*-PVPi-X stabilisers were found to have reduced solubility at higher molecular weights.

Determination of the stabilising ability of different molecular weight block copolymers in the dispersion of PNVP was determined using SEM (Figure 5.15).

The SEM micrographs show that the 11.9K stabiliser appears to give the most well-defined microsphere production. At 6.7K, although there is some evidence of particle formation, the overall product is a highly agglomerated structure. This is likely a result of an insufficient polymer chain length to ensure steric stabilisation and to prevent agglomeration. Again, this follows previous trends observed in Chapter 4, in which a 4.7K statistical copolymer stabiliser of 50:50 ratio was insufficient to produce well-defined spherical microparticles.

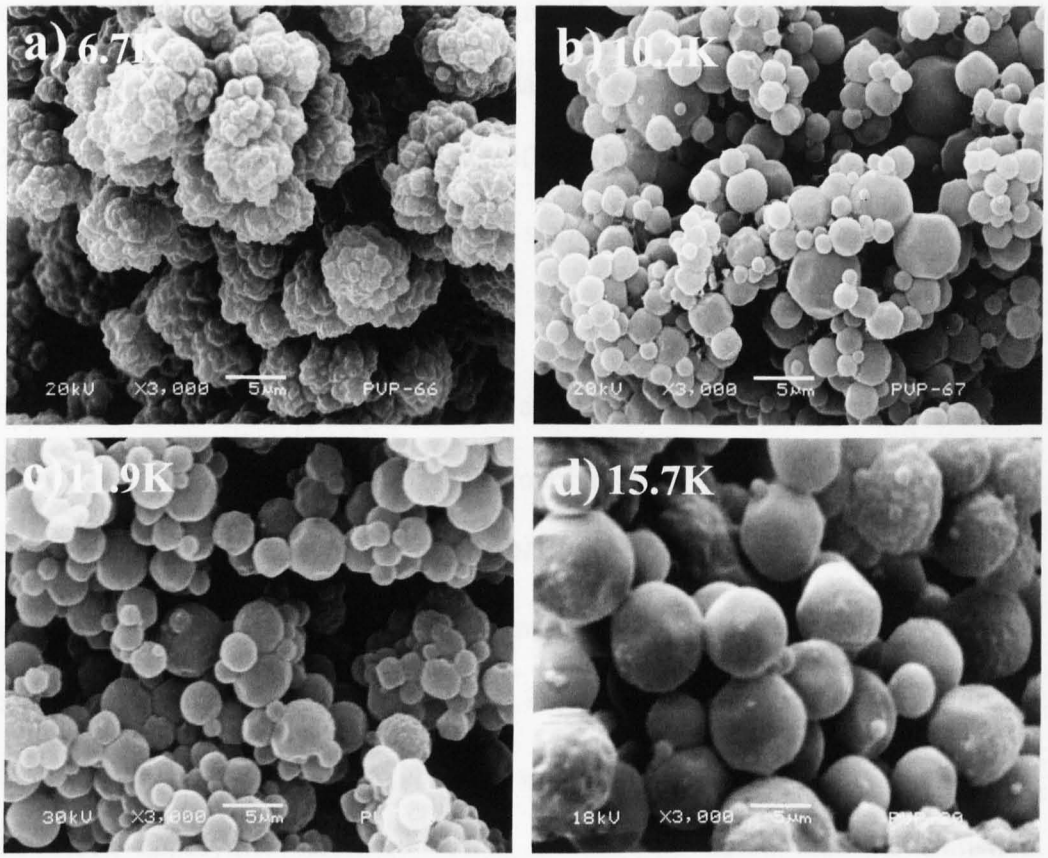


Figure 5.15: Comparison of PNVP products using block copolymer stabilisers of varying molecular weight. (a) 6.7K; (b) 10.2K; (c) 11.9K; (d) 15.7K. Data taken from Table 5.3, entries 5, 7, 8, 9.

Particle sizing data (Table 5.3, entries 5, 7, 8, 9) show that the average particle diameter (D_n) increases as the stabiliser molecular weight is increased. This is most likely a result of the decreasing number of individual polymer chains being employed within the dispersion as the stabiliser molecular weight is increased. Although 5 wt % of stabiliser is consistently employed for all reactions, as the molecular weight of the stabiliser is increased, the molar concentration within the

system will decrease. This means there are fewer stabiliser molecules (but of a higher molecular weight) which are available for interaction. This in turn means a decreased surface coverage as a result of fewer anchor points, and subsequently fewer growing PNVP particles will be stabilised, leading to the production of larger particles.

In all cases, the SEM micrographs show a broad distribution of particle sizes, and the C_V results confirm that the block copolymers at varying molecular weight continue to produce a wider range of PNVP microparticle diameters (Table 5.3, entries 5, 7-9 and columns 7-8). This indicates that compared to the statistical copolymers, the block copolymers result in less uniform particles. The results are similar to those obtained in the previous section when varying the composition of the block copolymer stabilisers. Also, it must be noted that the statistical copolymers do not exhibit the same trend, with particles of a similar diameter being obtained, leading to a narrow particle size distribution. As such this leads to the conclusion that this broader particle size distribution is related to the difference in stabiliser architecture.

Indeed, this broader particle size distribution can be explained when comparing the SEM images, which show a 'second crop' of particles, as mentioned in the previous section. This is particularly evident in the case of the 10.2K and 11.9K block copolymer stabilisers (Figure 5.15, b and c). The second crop of particles observed using the PVAc-*b*-PVPi-X block copolymer stabilisers accounts for the broader size distribution, and increased overall particle size diameter, as two crops of particles will affect the overall results.

Secondary particle generation can often occur in dispersion polymerisations. For example, Tseng *et al.* described the dispersion polymerisation of styrene in ethyl alchol.[56] The use of PNVP as a stabiliser in combination with an anionic surfactant Aerosol OT, a nonionic surfactant, Triton N-57, or cetyl alcohol as a co-stabiliser, resulted in a stable dispersion with narrow particle-size distribution (2.5-4.0 μm). However, without a co-stabiliser, dispersion with bimodal particle size distribution was obtained, and in addition to the main population of 3.2 μm in diameter, a population of larger particle sizes (4 to 15 μm) was found. These larger particles were presumed to form by coalescence of smaller particles during the particle growth stage.

Evidence of a second crop of polymer particles has also been observed in previous studies of dispersion polymerisations in $scCO_2$. Canelas *et al.* noted a similar effect in the SEM micrographs of PS particles synthesised *via* dispersion in $scCO_2$ utilising block copolymer stabilisers of PS and PFOA.[57, 58] In this case, the presence of a second, smaller crop of particles was attributed to a secondary nucleation process towards the end of the reaction. DeSimone *et al.* also reported evidence of a secondary particle formation when higher PFOA stabiliser concentrations were employed in the dispersion polymerisation of MMA.[59] This observation was attributed to excess stabiliser being able to support a second crop of smaller particles growing in the solution, but not yet captured by the larger particles. Conversely, Shaffer *et al.* noted a bimodal particle size distribution in the dispersion polymerisation of MMA using low weight percentages (<3.5 wt %)

of PDMS-mMA stabiliser, which was attributed to an agglomeration mechanism operating in the absence of sufficient stabiliser to protect the particle surface.[60, 61]

The bimodal particle size distribution observed when employing block copolymer stabiliser could be a result of insufficient stabilisation. The statistical copolymers clearly have an advantage over the block copolymers in this respect, as bimodal distributions are not observed. In addition, statistical copolymers are much more easily prepared than block copolymers, leading to the conclusion that statistical copolymers of PVAc and PVPi remain the most suitable for dispersion polymerisations of NVP in $scCO_2$.

5.3.2 Variation of Stabiliser End-group

Small variations in the end-group functionality of surfactant materials have been known to effect changes in both $scCO_2$ solubility and stabilising ability.[62-64] Hydrocarbon stabilisers with different end-groups were synthesised and studied in order to determine the effect on solubility and the importance of the end-group in acting as the polymeric anchoring functionality. This section details some initial studies, and probes the effect of anchor group on both phase behaviour and dispersion polymerisation in $scCO_2$.

5.3.2.1 Variation of Xanthate R Group

The R group of the RAFT agent is known as the leaving group. This group must be capable of leaving the polymer by undergoing homolytic scission, and should also be able to reinitiate polymerisation.[1] In this section, two stabilisers were initially synthesised using xanthates with slightly different R groups. This enabled incorporation of different functionality into the α-end of the polymeric stabiliser. While it is assumed that the Z group of the stabiliser is the portion which acts as the anchoring group of the material, it is still of interest to determine how, if at all, this difference in the R group will affect the stabiliser.

Xanthates X1 and X2 were both employed in the RAFT polymerisation of VAc and VPi to obtain statistical copolymers for comparison (Figure 5.16).

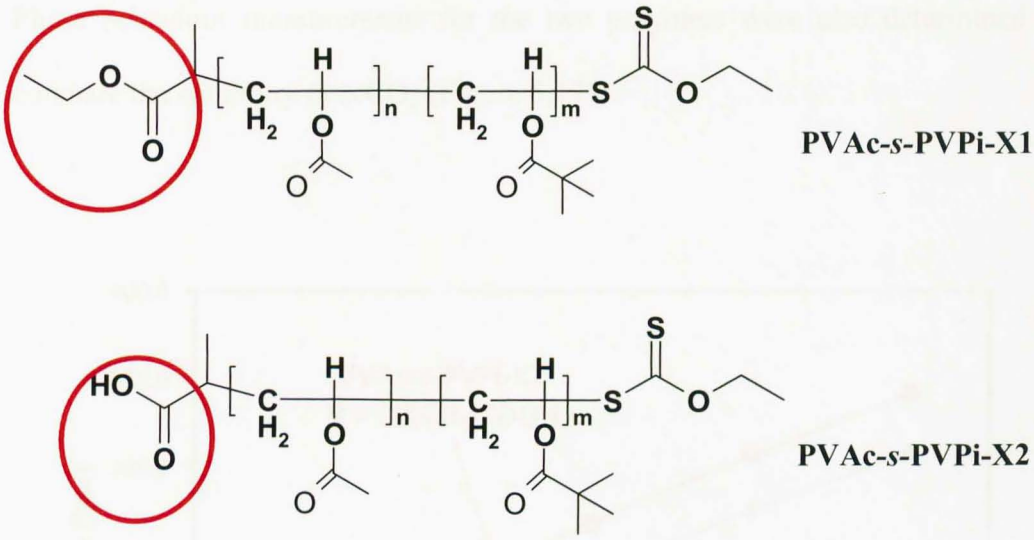


Figure 5.16: Structures of polymers synthesised using Xanthate X1 and X2.

The two resulting polymers chosen for comparison were of similar composition and molecular weight, and consequently had relatively similar polymer chain lengths (Table 5.4).

Table 5.4: Polymer synthesised using xanthate X1 and X2.

Polymer End-Group	$M_{n,expt}$ (kg/mol)[a]	PDI[a]	Ratio (PVAc:PVPi)[b]	DP[c]	Cloud Point (bar)[d]
R = $CH(CH_3)CO_2Et$ (X1)	9.4	1.45	54:46	83	163
R = $CH(CH_3)COOH$ (X2)	10.5	1.50	54:46	89	185.2

[a]Experimental M_n and PDI obtained from GPC-RI detector using THF eluent and PS standards. [b]Ratio determined from ^1H NMR in $CDCl_3$. [c]Degree of polymerisation calculated using M_n and ratio. [d]Cloud point at 35 °C determined using variable volume view cell.

Phase behaviour measurements for the two polymers were also determined to compare the solubility in $scCO_2$ (Figure 5.17).

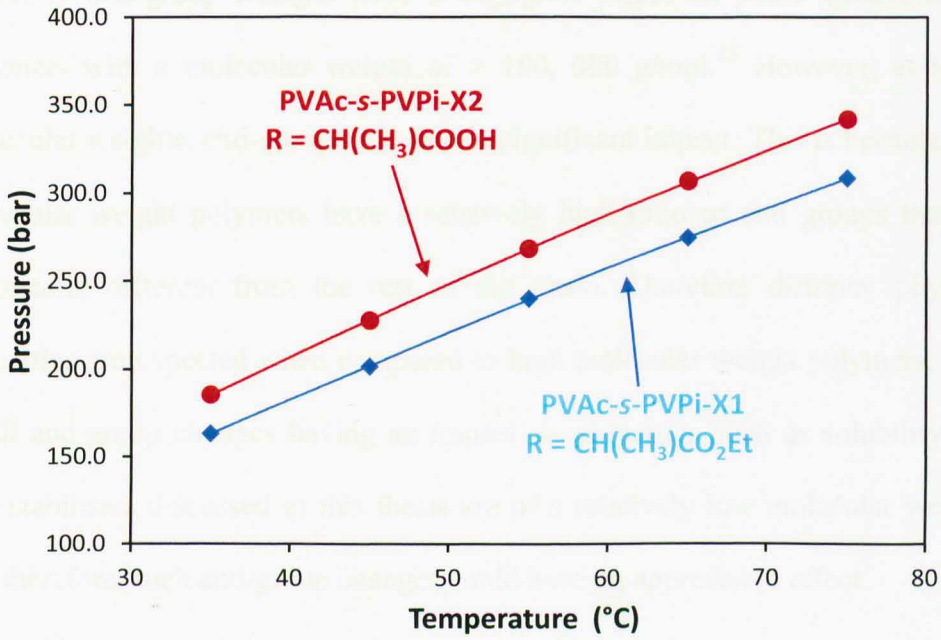


Figure 5.17: Phase behaviour of copolymer stabilisers with varying α-end-group as a result of adjusting the initial xanthate employed (Table 5.4, entries 1-2). Cloud point pressures were measured three times and an average was used, accurate to ±0.5-1.0 bar.

The phase behaviour curves of the two stabilisers show that the X1 capped polymer has improved solubility compared to that of the polymer synthesised using X2. The data show that incorporation of different end-groups result in a stabiliser which is significantly less soluble, despite the change in end-group only

being a very small change to the structure. This variation in solubility is too significant to be attributed to experimental error alone, and must be a result of the differences in polymer end-group.

Typically end-group changes have a negligible effect on phase behaviour for polymers with a molecular weight of > 100, 000 g/mol.[65] However, at lower molecular weights, end-groups can have a significant impact. This is because low molecular weight polymers have a relatively high ratio of end groups that are chemically different from the rest of the chain. Therefore different physical properties are expected when compared to high molecular weight polymers, with small end-group changes having an impact on properties such as solubility.[66-68] The stabilisers discussed in this thesis are of a relatively low molecular weight, and therefore, such end-group changes could have an appreciable effect.

Comparison of PVAc-*s*-PVPi-X1 and PVAc-*s*-PVPi-X2, shows that X2 solubility is significantly decreased and there is a large discrepancy in the cloud points of the two materials, indicating that the presence of the –COOH moiety must be causing this effect.

This is likely related to the fact that xanthate X2 incorporates a polar –COOH group into the polymer structure. Polarity is known to reduce solubility in $scCO_2$ and the introduction of polarity by the carboxylic acid group has a negative impact on the CO_2-solubility.[64, 69] The opportunity for inter- and intra-molecular hydrogen bonding is increased as a result of the introduction of a polar end-group, and as a result the dissolution of the polymer in CO_2 is hindered, and the observed

cloud point pressures are higher. A similar effect has been observed by Drohmann *et al.*, who observed that the solubility of poly(alkylene glycol)s in CO_2 was improved by the end-capping of one or both of the hydroxyl end-groups by alkyl groups.[64]

Following the measurement of phase behaviour for the two stabilisers, the stabilising ability of the materials was tested in dispersion polymerisations in $scCO_2$ using NVP monomer and 5 wt % stabiliser (Table 5.5).

Table 5.5: Dispersion Polymerisations in $scCO_2$.

Stabiliser		PNVP Product				
Polymer End-group	**Cloud Point (bar)[a]**	**M_w (kg/mol)[b]**	**PDI[b]**	**D_n (μm)[c]**	**C_V (%)[d]**	**Yield (%)[e]**
R = $CH(CH_3)CO_2Et$ (X1)	163.0	231	5.4	2.4	25.2	89
R = $CH(CH_3)COOH$ (X2)	185.2	225	5.1	2.2	37.9	83

Polymerisation conditions: $scCO_2$ polymerisation at 35 °C for 48 hours with V-70 initiator and 5 wt % of stabiliser. [a]Stabiliser cloud point determined at 35 °C using variable volume view cell. [b]Experimental M_w and PDI obtained from GPC-RI detector in chloroform with 5 % triethylamine using PS standards. [c]Mean particle diameter as determined from sampling of ~100 particles of a typical SEM image. [d]Coefficient of variance as determined by equation $C_v = (\sigma/D_n) \times 100$. [e]Yield determined gravimetrically.

High pressure polymerisations resulted in high molecular weight powder products for each of the stabilisers employed. Analysis of morphology through comparison of the SEM micrographs shows the effect of the reduced solubility of PVAc-*s*-PVPi-X2, as the stabilising ability appears to be reduced to some extent (Figure 5.18).

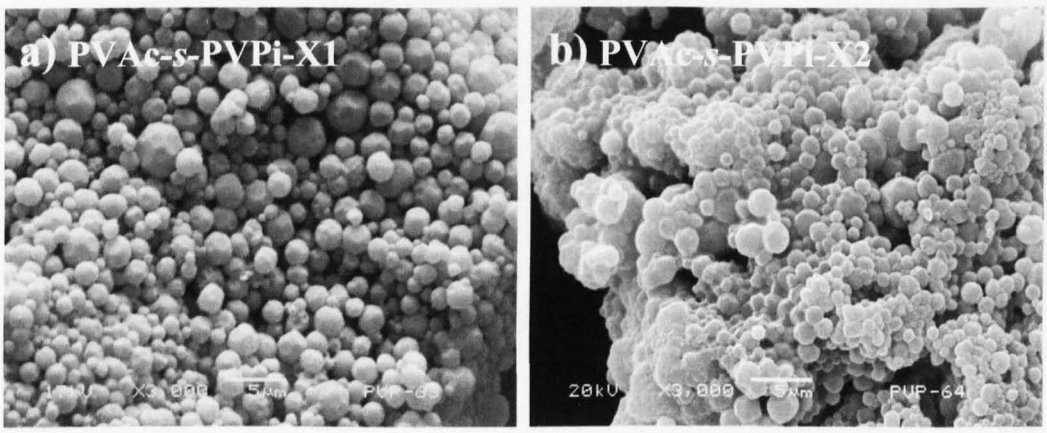


Figure 5.18: Effect of employing two different xanthates for stabiliser synthesis, resulting in variation of the α-end-group on PNVP product. (a) PVAc-*s*-PVPi-X1 with R = $CH(CH_3)CO_2Et$; (b) PVAc-*s*-PVPi-X2 with R = $CH(CH_3)COOH$.

Fewer well-defined, spherical particles are formed and increased agglomeration and distortion is observed in the case of the PVAc-*s*-PVPi-X2 stabiliser (Figure 5.18, b). In addition, particle sizing indicates that the C_v is higher for PVAc-*s*-PVPi-X2 surfactant, showing that a broader range of diameters are present within the sample. Overall, the introduction of the –COOH end-group does appear to

make some difference to both the stabilising ability and solubility, although this difference is not so significant as to completely hinder the dispersion polymerisation, and high conversion with spherical particle morphology is still obtained.

5.3.2.2 Radical-induced Reduction of Polymers

In this section, radical-induced reduction has been targeted as a means of cleaving the xanthate end-group functionality from the hydrocarbon polymer stabiliser. The removal of this group from the stabiliser structure is of interest, in order to determine the impact of the RAFT end-group, and consequently the anchor group of the stabiliser, on the dispersing ability in $scCO_2$.

Radical-induced reduction allows the thiocarbonylthio group of RAFT-synthesised polymers to be replaced with a hydrogen atom. The process involves thiocarbonylthio compounds undergoing facile reaction with radicals by addition–fragmentation.

The mechanism of radical-induced reduction involves the production of a radical species (X•), which then adds to the thiocarbonyl group of the macro-RAFT agent. This species then fragments to provide a propagating radical and a new thiocarbonylthio compound. Reaction of the propagating radical with a hydrogen atom donor (H-X) then gives the desired product in which the thiocarbonylthio group has been replaced with hydrogen. This process is a radical chain reaction and is catalytic in X•.[18, 19, 49] Both PVAc-*s*-PVPi-X1 and PVAc-*s*-PVPi-X2 terminated polymers were reduced using *N*-ethylpiperidine hypophosphite (EPHP), the mechanism of which is outlined in Figure 5.19.

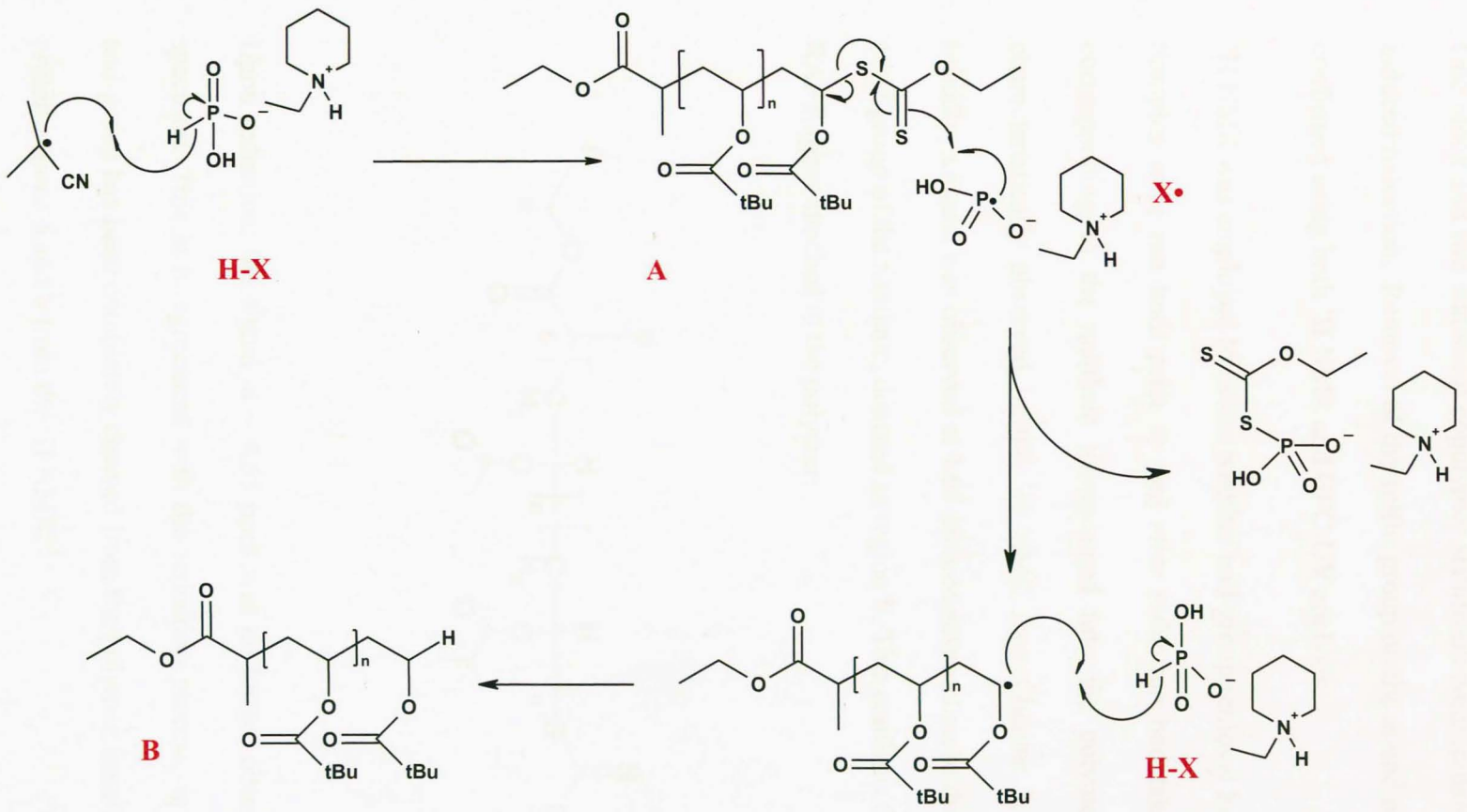
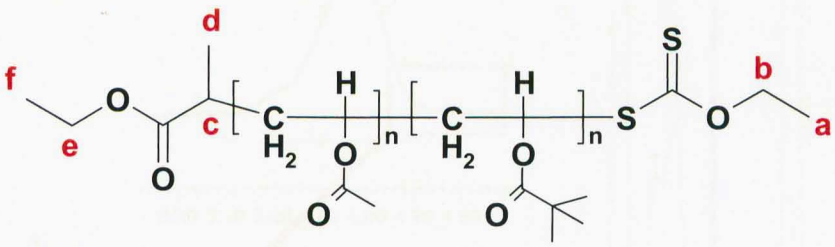


Figure 5.19: Mechanism of radical-induced reduction. Overall the RAFT functionality of polymer A is reduced by a hydride terminating group to form polymer B.

One block and two statistical copolymer stabilisers were transformed *via* radical-induced reduction. Removal of the sulfur group on the ω-end of the polymer was confirmed using both ^{1}H NMR and GPC-UV analysis.

^{1}H NMR was employed to assess whether end-group removal had been successful. Samples were run both prior to and after reduction had taken place. Signals corresponding to the xanthate incorporated into the polymeric stabiliser are characteristically observed in the ^{1}H NMR (see Chapter 3, section 3.2.3.1). Initially, a signal was observed at 4.65 ppm corresponding to the protons from the ethyl group of the xanthate, denoted as region **b**. This confirms the presence of the RAFT agent attached to the polymer.



Upon reduction, the signal at ~ 4.65 ppm was no longer observed in the NMR spectrum. This is in agreement with the reduction process, in which the sulfur end-group has been completely cleaved from the polymer, resulting in removal of proton regions **a** and **b** from the ^{1}H NMR.

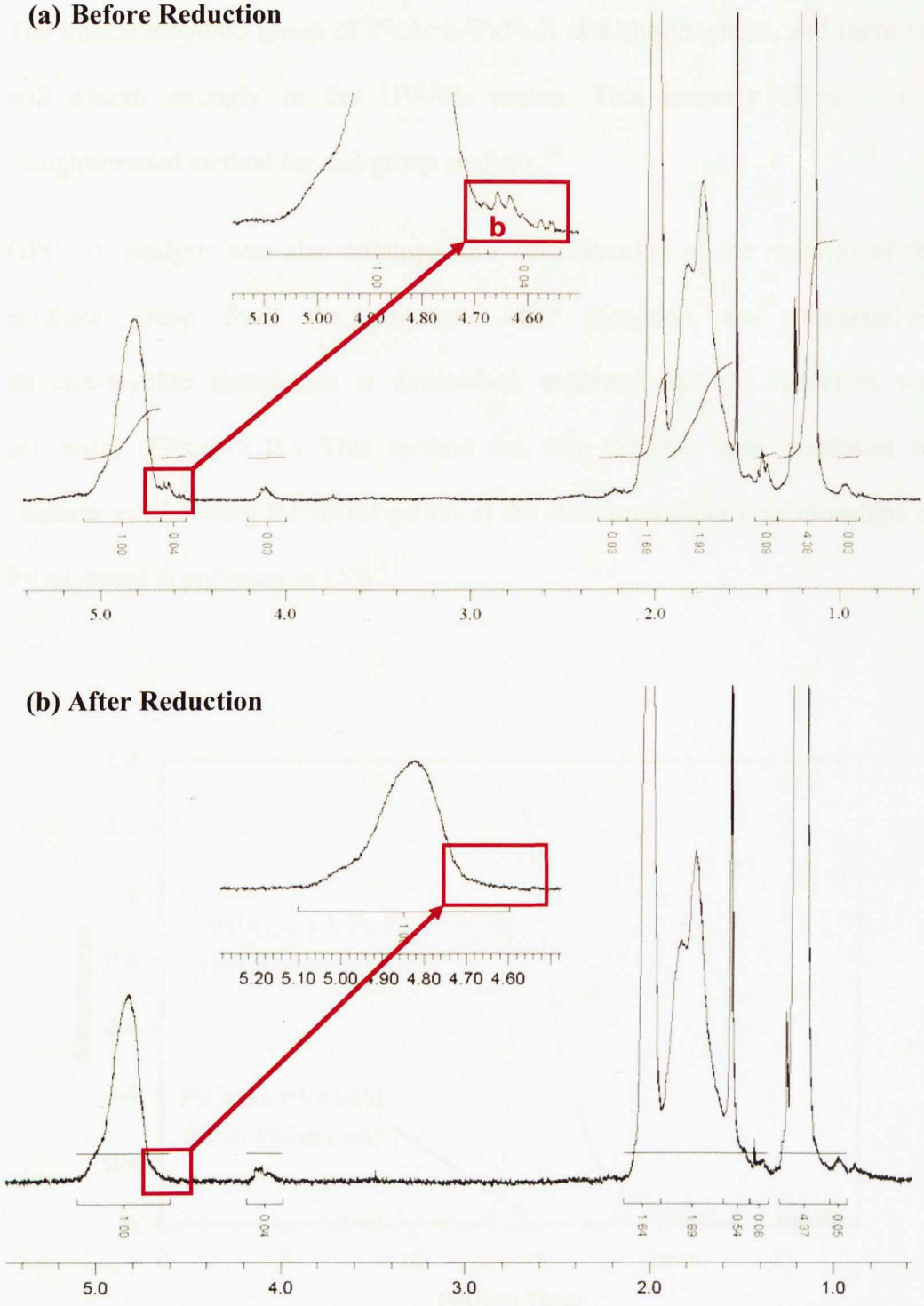


Figure 5.20: ^{1}H NMR of stabiliser (a) prior to and (b) after reduction. Peaks corresponding to xanthate end-group are completely removed after reduction.

The thiocarbonylthio group of PVAc-*s*-PVPi-X is a chromophore, and therefore will absorb strongly in the UV-Vis region. This property allows for a straightforward method for end-group analysis.[70]

GPC-UV analysis was also employed for determination of the removal of the xanthate group from the polymer. After reduction, the characteristic thiocarbonylthio absorbance is diminished, evidence that the reduction was successful (Figure 5.21). This method has also recently been employed by Destarac *et al.* during the investigation of the structure-property relationships of PVAc-based copolymers in CO_2.[71]

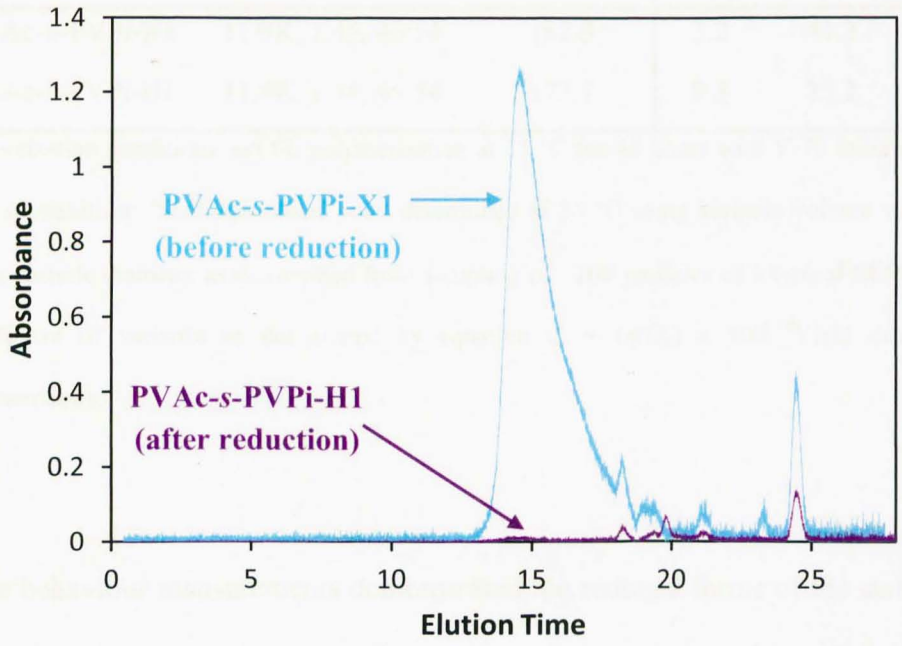


Figure 5.21: Characteristic sulfur absorbance present at 254 nm prior to reduction and absent in trace after radical-induced reduction.

The phase behaviour and stabilising ability of both the initial and reduced forms of the stabilisers was determined and compared (Table 5.6).

Table 5.6: Comparison of Initial and Reduced Forms of PVPi-based Stabilisers.

Stabiliser			PNVP Product		
Polymer	**M_n, PDI, Ratio**	**Cloud Point (bar)[a]**	**D_n (μm)[b]**	**C_V (%)[c]**	**Yield (%)[d]**
PVAc-*s*-PVPi-X1	9.4K, 1.45, 54:46	163.0	2.4	25.2	89
PVAc-*s*-PVPi-H1	8.8K, 1.40, 54:46	148.1	3.7	42.9	84
PVAc-*s*-PVPi-X2	10.5K, 1.50, 54:46	185.2	2.2	37.9	83
PVAc-*s*-PVPi-H2	10.4K, 1.53, 54:46	176.1	2.7	42.6	79
PVAc-*b*-PVPi-X1	11.9K, 1.45, 46:54	182.8	3.2	41.2	82
PVAc-*b*-PVPi-H1	11.9K, 1.44, 46:54	173.7	9.3	23.2	87

Polymerisation conditions: $scCO_2$ polymerisation at 35 °C for 48 hours with V-70 initiator and 5 wt % of stabiliser. [a]Stabiliser cloud point determined at 35 °C using variable volume view cell. [b]Mean particle diameter as determined from sampling of ~100 particles of a typical SEM image. [c]Coefficient of variance as determined by equation $C_v = (\sigma/D_n) \times 100$. [d]Yield determined gravimetrically.

Phase behaviour measurements demonstrated the reduced forms of the stabilisers to be more soluble in $scCO_2$, by ~ 10-20 bar (Figure 5.22). This was expected, because of the removal of the polar sulfur component, which subsequently improved solubility of the polymer. This is in contrast to the work of Destarac *et al.*, in which solubility experiments were carried out, comparing $PVAc_{3.8K}$–Xa

and a xanthate-free equivalent, $PVAc_{4.2K}$–H, obtained by a radical-induced reduction of the xanthate group. No substantial differences in the solubility in $scCO_2$ were observed and the polymers were found to be respectively soluble in proportions of 0.89 wt% and 0.87 wt% at 35 MPa.[71]

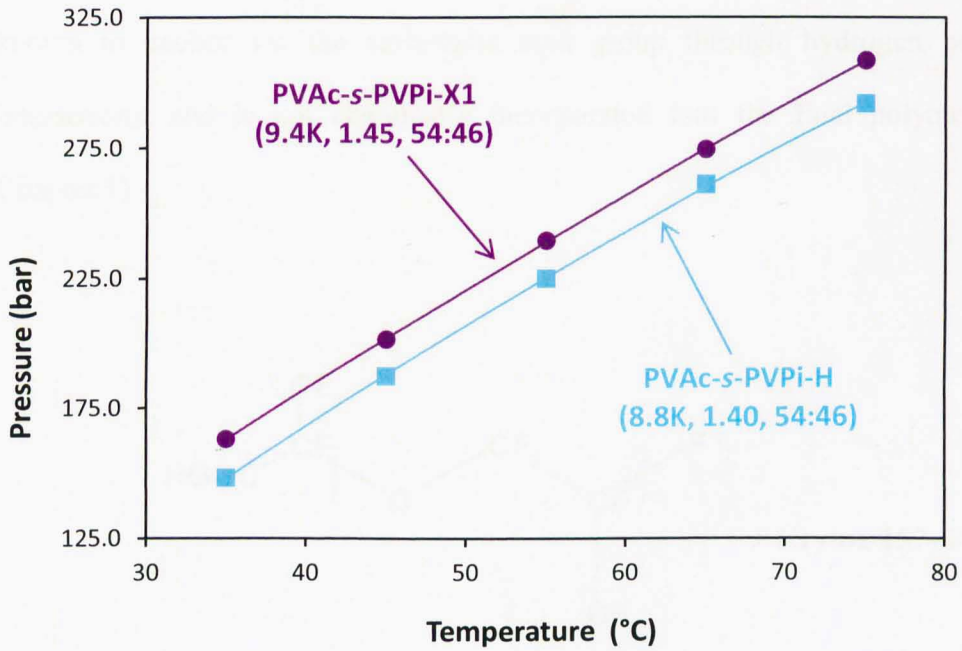
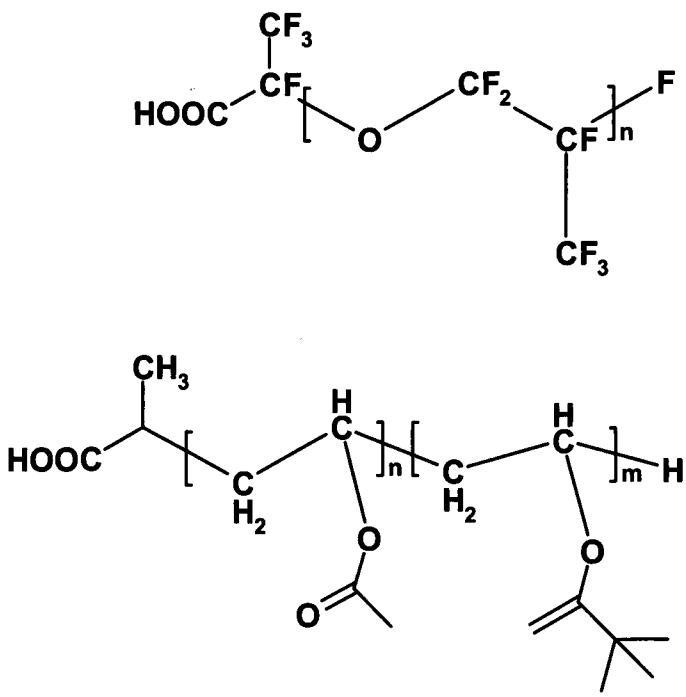


Figure 5.22: Phase behaviour of PVAc-*s*-PVPi-X stabiliser and the reduced form PVAc-*s*-PVPi-H (Table 5.6, entries 1-2). Cloud point pressures were measured three times and an average was used, accurate to ±0.5-1.0 bar.

Each of the H-terminated polymers were employed in the polymerisation of NVP in $scCO_2$. It was expected that PVAc-*s*-PVPi-X1, once reduced to the hydrogen

form, would be unsuccessful in all polymerisations, because of the lack of an anchor group. In the case of PVAc-*s*-PVPi-X2, the reduced form of the stabiliser resembles a hydrocarbon version of the Krytox-157 FSL structure (Figure 5.23). Therefore, it might also be possible that the –COOH α-end of the polymer could potentially act as an anchor in a similar manner to that of Krytox-157 FSL, and stabilise either NVP or MMA polymerisations in $scCO_2$. Krytox-157 FSL is known to anchor *via* the carboxylic acid group through hydrogen bonding interactions, and is not chemically incorporated into the final polymer (see Chapter 1).



Krytox 157- FSL

PVAc-*s*-PVPi-H2

Figure 5.23: Structure of Krytox stabiliser, and the reduced form of PVAc-*s*-PVPi-X2. Both structures are similar, and are soluble in $scCO_2$.

These results indicated that a range of stabilisers with no xanthate end-group present were all able to support dispersion polymerisation to the extent that a free flowing powder product with high conversion was obtained. However, the defined spherical microparticle structure characteristic of the RAFT synthesised stabilisers was not present when using a stabiliser with a reduced end-group. This suggests that the xanthate component of the stabiliser does play a significant role in successfully anchoring to the growing polymer particle. Some form of stabilisation is clearly present with the reduced polymers, as observed by the production of high yielding powder products, but there are likely to be differences in the mechanism by which the stabiliser anchors to the PNVP particles, leading to differences in the control over particle morphology.

Whilst PVAc-*s*-PVPi-X stabilisers appear to be anchoring by chemically interacting with the PNVP particles, as a result of the compatible xanthate RAFT agent attached to the stabiliser, PVAc-*s*-PVPi-H does not possess this group and therefore must interact in another way. The presence of the –COOH group at the α-end of the polymer also does not appear to be sufficient to provide stabilisation equivalent to Krytox-157 FSL, leading to ill-defined particle morphology (Figure 5.24, c). This suggests that a hydrogen bonding mechanism of anchoring to the growing PNVP particles through the –COOH group is unsuccessful for the hydrocarbon stabilisers. The differences between Krytox-157 FSL and the PVAc-*s*-PVPi-H2 equivalent are likely a result of the differences in polarity, and the lack of fluorinated groups, which has a significant impact on the stabilising ability.

Polymerisation of NVP in $scCO_2$

The polymerisation of NVP in $scCO_2$ was conducted using the reduced stabilisers and compared with the polymerisation results using the initial forms of the polymers (Table 5.6, column 4-6). All polymerisations resulted in a free-flowing powder product and comparable conversions. SEM analysis showed that discrete microparticle formation was not observed using the reduced stabilisers (Figure 5.24, b-d) in comparison to the RAFT-terminated stabiliser (Figure 5.24, a).

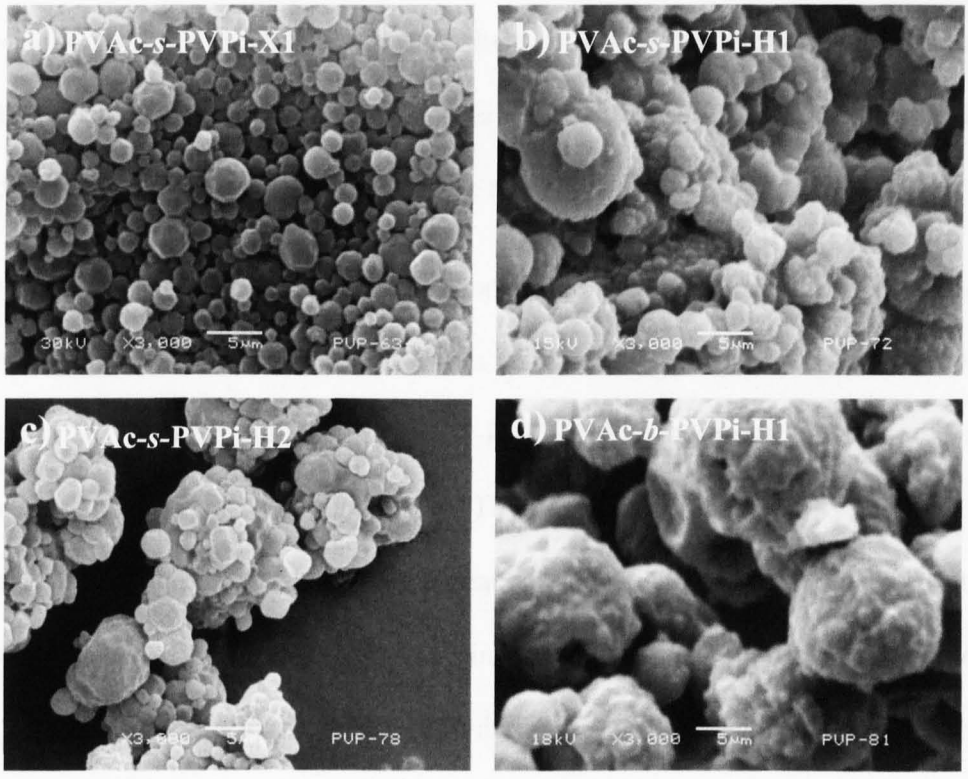


Figure 5.24: SEM micrographs of PNVP microparticles synthesised using PVAc-*s*-PVPi-H stabilisers: a) PVAc-*s*-PVPi-X1; b) PVAc-*s*-PVPi-H1; c) PVAc-*s*-PVPi-H2; d) PVAc-*b*-PVPi-H1. Data obtained from Table 5.6; entries 1, 2, 4 and 6 respectively.

It is also important to note the reduced forms of the polymers are still an improvement on the use of stabilisers synthesised by a typical free radical polymerisation method, which are unable to support dispersion polymerisation of NVP in $scCO_2$ to any extent (see Chapter 4). Therefore, the RAFT polymerisation process remains a key technique for synthesising successful PVPi-based hydrocarbon stabilisers which are able to aid dispersion polymerisations in $scCO_2$.

Although little control over particle morphology is observed using the reduced stabilisers, PNVP is still obtained as a free-flowing powder product with a high yield in all cases, despite the lack of the RAFT end-group. These results suggest that some degree of stabilisation is still taking place.

PFOA is an amphipathic polymeric stabiliser that contains an acrylic-like backbone, which is CO_2-phobic.[59, 72, 73] In the case of this type of stabiliser, it is the backbone of the stabiliser material which physically or chemically anchors to the growing polymer particle. Particle flocculation is prevented by the fluoralkyl side chains, which project into the continuous phase and provide steric stabilisation. It is possible that although the copolymer stabilisers described in this section do not possess a xanthate-based anchor group, some form of stabilisation could be provided through a weak physical adsorption *via* the backbone of the stabiliser (Chapter 4, Figure 4.10, b). This could account for the differences observed in the dispersion polymerisations when employing the two types of stabiliser end-groups, as two different anchor mechanisms are involved. It would also explain the reason for free-flowing, powder polymers being obtained in the case of the cleaved stabilisers, where there is no RAFT-terminated polymer to act

as the anchor group. However, further investigation of the anchor group theory and the results obtained in this section is still required before a definitive conclusion can be drawn. It is also possible that the RAFT-terminated stabilisers do not even act as anchors as is hypothesised (Chapter 4, Figure 4.10, a) and this is also something that needs to be considered more carefully.

One possibility for additional research on the anchor group could involve a series of experiments to determine whether the PVPi-based stabilisers are chemically grafted onto the PNVP polymers. This could be carried out *via* $scCO_2$ extraction of the PNVP sample, with the aim of removing any stabiliser which is not chemically bound to the polymer particles. Comparison of NMR before and after extraction should give an indication of whether the stabiliser is still retained, and therefore grafted to the PNVP. This method could be applied to both the xanthate-capped and cleaved versions of the stabiliser, to determine if they are any differences in the proportion of stabiliser chemically bound to the PNVP. Soxhlet extractions could also provide useful in the determination of whether the stabiliser is anchoring *via* the RAFT agent. The use of analytical techniques to probe the interaction of the stabilisers with the surfaces of the growing PNVP particles in $scCO_2$ would also provide key information about these systems.

Polymerisation of MMA in $scCO_2$

In addition, attempts to polymerise MMA in $scCO_2$ using both the reduced and xanthate terminated stabilisers were considered. These polymerisations were largely unsuccessful, resulting in low conversion.

For the xanthate terminated stabilisers, such observations are attributed to the fact that VAc, a less activated monomer, is a poor leaving group in comparison to MMA, a more activated monomer.[1] As a result, the initiated MMA will leave the RAFT agent in preference to VAc, and chain extension of MMA *via* the stabiliser cannot take place. Therefore, only precipitation polymerisation of MMA will occur.

However, following cleavage of the xanthate end-group, polymerisations continued to be unsuccessful. This indicates that the stabilisers cannot anchor to the growing PMMA particles sufficiently, with or without the xanthate end-group, and so cannot produce a dispersion system for MMA in $scCO_2$. A different RAFT end-group would be a possible solution to this barrier, where manipulation of the anchor group could potentially favour increased reactivity towards subsequent propagation of MMA, whilst still incorporating a RAFT functionality capable of acting as the anchor. This is an aspect of research that is currently being considered to extend the applications of the hydrocarbon stabilisers.

5.4 Conclusions

The work presented in this chapter has shown that a range of stabiliser architectures can be synthesised, and that these polymeric materials will stabilise polymerisations in $scCO_2$ to varying extents.

The first section of the chapter dealt with the synthesis of block copolymers of PVAc and PVPi *via* the RAFT polymerisation technique. A range of block copolymers of varying composition and molecular weight were produced, and their solubility determined. Block copolymer architectures were observed to be less soluble than comparable statistical copolymer stabilisers, which was attributed to the segregated arrangement of the VAc and VPi components. Application of the block copolymers in the polymerisation of NVP in $scCO_2$ resulted in successful polymerisations with high conversion. In addition, characterisation using SEM analysis revealed the production of discrete, spherical microparticles. However, it was also observed that these particles were larger in diameter than those obtained using statistical copolymer stabilisers, and also possessed a broader particle size distribution.

The second section of the chapter involved end-group transformations of the polymeric stabiliser. Incorporation of a polar α-end-group into the structure led to decreased solubility and less uniform polymer particles. Radical-induced reduction of a selection of stabilisers was also carried out, leading to the production of polymers free of the RAFT end-group. All of the subsequent H-capped polymers were found to be slightly more soluble than the polymers

retaining the xanthate end-group. Further to this, the H-capped stabilisers were employed in polymerisations of NVP in $scCO_2$ and found able to stabilise to some extent. Upon SEM analysis, it was observed that the resulting particle morphology was ill-defined and irregular. This demonstrated that although polymers without the xanthate group will function as stabilisers to some degree, and stabilise the growing PNVP particle in $scCO_2$, the polymers clearly do so to a much lesser extent.

Whilst this chapter has sought to identify the means by which the architecture can be varied, there is much additional work to be completed in this area. Variation of the end-group functionality, and understanding the way in which the anchoring group of the PVPi-based polymers work could be the key to extending the range of monomers suitable for use with these stabilisers. Application of these materials to the polymerisation of other monomers in $scCO_2$, such as styrene and MMA, is the next challenge which must be addressed if PVAc-PVPi-X stabilisers, are to be considered as commercially viable hydrocarbon stabilisers.

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Chapter 6: Conclusions and Future Research

The final chapter of this thesis outlines the overall conclusions obtained from the research presented, and summarises the potential of this class of PVPi-based polymers to act as CO_2-soluble hydrocarbon stabilisers.

The chapter also discusses possible aspects of investigation for the continuation of the work, if research on PVPi hydrocarbon stabiliser synthesis were to be continued.

6.1 Conclusions

Throughout the course of this thesis, the development of CO_2-soluble polymers composed primarily of hydrocarbon substituents has been investigated. The synthesis of these materials has been undertaken by exploiting the RAFT polymerisation technique to produce well-defined polymers with a controlled molecular weight and specific architecture. The ability of these polymers as stabilisers for dispersion polymerisation in $scCO_2$ has been considered and evaluated.

6.1.1 Synthesis and Solubility of PVPi-based Stabilisers for $scCO_2$

In Chapter 3, a series of homopolymer and statistical copolymer stabilisers composed of the monomers VAc and VPi were synthesised. The polymers were produced using xanthate-based RAFT polymerisation, affording controlled molecular weight polymers with a reasonable PDI. A series of polymers with both a range of molecular weights and compositions were targeted and fully characterised.

The VPi-based polymeric materials were subsequently evaluated for solubility in $scCO_2$, using a high pressure variable volume view cell. In all cases, it was observed that the VPi moiety provided a high degree of CO_2-solubility. For the VPi homopolymers, solubility was observed to decrease with increasing D_p, and subsequent chain length. Statistical copolymers of VAc and VPi units were found to be significantly more soluble than the corresponding homopolymers of similar

chain length, and an increased VPi content led to improved solubility. In addition, the effect of PDI, co-solvent and use of monomer alternatives to VAc were assessed. PDI was shown to have some impact on the solubility of the polymer, and co-solvent had a significant effect on improving CO_2-solubility. The monomers VPr and IPAc were found to provide little improvement on the PVAc-*s*-PVPi-X copolymer stabilisers.

Finally, a copolymer of PVAc and PVPi was also synthesised using free radical polymerisation in the absence of a RAFT agent, to determine whether RAFT polymerisation was indeed required to obtain effective stabilisers. The cloud point was dramatically reduced when compared to a RAFT synthesised copolymer, as a result of the significant increase in PDI. RAFT polymerisation was observed to be an effective technique for targeting stabilisers of controlled molecular weight and narrow PDI, able to provide enhanced CO_2-solubility.

Overall, polymers composed of PVAc and PVPi were successfully synthesised using RAFT polymerisation, producing stabilisers with a RAFT end-group. These polymers were determined to be highly CO_2-soluble, with potential for application as stabilisers in $scCO_2$.

6.1.2 Dispersion Polymerisation using Hydrocarbon Stabilisers

Chapter 4 described the application of the hydrocarbon polymers synthesised and characterised in the previous chapter as stabilisers in $scCO_2$. The polymers were employed in the dispersion polymerisation of NVP in $scCO_2$, and their stabilising

ability was compared by contrasting product yield, appearance and particle morphology. The PVPi-based stabilisers were observed to act as highly efficient stabilisers, enabling the production of a polymer powder of high yield with relatively uniform, spherical microparticles, which varied to some extent as the composition was adjusted. Increasing the proportion of PVAc in the statistical copolymers was found to lower CO_2-solubility, whilst also producing smaller particles. Molecular weight of the stabiliser was also found to affect the dispersion polymerisation, attributed to the lack of steric stabilisation imparted when the D_p, and subsequent chain length, of the stabiliser was lowered. Stabiliser loading was also observed to have an impact, and the polymers functioned successfully as stabilisers even at modest values. However, a reduced particle size and improved morphology were observed when increased stabiliser loadings were employed.

A free radical copolymer was also compared with a RAFT synthesised equivalent, and found to be unsuccessful for supporting dispersion polymerisation, leading to low yielding PNVP product with no distinct particle morphology. This was determined to be a result of both the lack of anchor group in the stabiliser structure, and also the impact of the broad molecular weight distribution. Therefore, it was concluded that RAFT polymerisation is crucial for obtaining targeted, narrow molecular weight distributions with a specific anchor group in the form of the sulfur end-group incorporated during the process of the RAFT polymerisation mechanism.

Additionally, the synthesis of PVPi-based stabilisers in $scCO_2$ was attempted, in order to determine whether the use of organic solvents could be completely eliminated in the preparation of such materials. Success was limited, and attributed in part to the polymerisation conditions, and the length of the reaction.

6.1.3 Investigation of Poly(vinyl pivalate) Copolymer Architecture

Finally, Chapter 5 dealt with the synthesis, characterisation and application of stabilisers with different architectures. This section can be classified into two main parts.

The first part dealt with the synthesis and characterisation of block copolymers of PVAc and PVPi. A comparison of the phase behaviour and stabilising ability of block and statistical copolymers was investigated. Block copolymer architectures were observed to possess decreased solubility in $scCO_2$ compared to random copolymer equivalents. This was proposed to be an effect of the segregation of the PVAc and PVPi segments, resulting in the favourable properties of the two monomers not being fully exploited throughout the length of the stabiliser structure.

The second section explored the effect of the stabiliser end-group on phase behaviour and dispersion activity in $scCO_2$. This was first investigated through a few adjustments to both the α- and ω-end of the polymeric stabiliser.

Initially, incorporation of a more polar α-end-group into the polymer was investigated, and synthesised through adjustment of the xanthate-based CTA employed in the RAFT polymerisation. The increased polarity was observed to have a negative impact on both phase behaviour and stabilising ability, leading to higher cloud point pressures and ill-defined PNVP polymer particles following their application in dispersion polymerisation.

The sulfur moiety of the hydrocarbon stabiliser was completely removed using radical-induced reduction, and the effect of H-capping the stabiliser was considered.[1] Removal of the sulfur end-group from the stabiliser led to a small improvement in the CO_2-solubility. Whilst the stabilising ability was found to be limited and ill-defined PNVP particle morphology obtained, it was interesting that any stabilisation was observed at all despite the absence of the portion of the stabiliser previously assumed to be the polymer-philic anchor group. The observation of some degree of stabilisation using H-capped stabilisers has not been fully considered in this work, but could be a result of weak physical adsorption of the polymeric stabiliser to the growing polymer particles, as observed using other stabilisers.[2]

6.2 Future Research

This section aims to identify avenues of research which would continue to further the knowledge built upon thus far in this thesis. A few key aspects of potential future work are highlighted, which were not able to be considered fully in this thesis due to time limitations, but could provide exciting areas for future research.

6.2.1 Further Investigation of Vinyl Pivalate Stabilisers

Although the work detailed within this thesis has demonstrated the potential of stabilisers composed of VPi, there are still a number of areas which need to be considered further. A mechanistic understanding of the interaction of the hydrocarbon stabilisers with PNVP is crucial in furthering the research using these materials. It is important to determine whether the RAFT end-group is necessary for a successful dispersion, and if it is chemically involved in anchoring to the growing particles, and further to this, whether it is possible to stabilise dispersion polymerisations without the anchor group. A number of techniques could be applied in the future to probe the mechanism of anchoring, some of which have already been discussed in Chapter 5.

Use of alternative polymerisation techniques such as Catalytic Chain Transfer (CCT) could also be a possible method for synthesising statistical copolymer stabilisers with the potential to act as stabilisers, and this would also test whether the incorporated RAFT group is required, while also affording some degree of molecular weight control.

6.2.2 New CO_2-soluble Monomers for Hydrocarbon Stabiliser Design

Whilst the PVAc-*s*-PVPi-X hydrocarbon stabilisers synthesised in this thesis show improved solubility in $scCO_2$ compared to other hydrocarbon polymers to date, there still exists potential for further improvement. Testing the phase behaviour of other, new hydrocarbon polymers might reveal other potential stabiliser materials, and also improves the understanding of the properties required to impart favourable CO_2-solubility on a material.

Polymers composed of VPi have been identified as highly CO_2-philic, resulting from the increased steric bulk of this monomer when compared to the less sterically hindered equivalent, VAc.[3] Another possible monomer to consider for copolymerisation with VAc is that of vinyl neodecanoate (VnDc) (Figure 6.1). This monomer is even more sterically hindered than VPi, and because of this could further increase the free volume of the polymer in $scCO_2$, minimising interactions between the individual polymer chains.

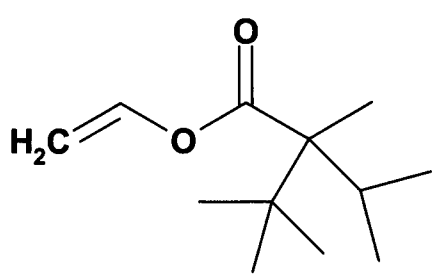

Figure 6.1: Structure of the monomer vinyl neodecanoate, VnDc.

Beyond poly (vinyl alkanoates) as stabilisers, it is likely there are other hydrocarbon polymers which could easily be adapted for use as stabilisers for dispersion polymerisations in $scCO_2$. A limited amount of research has already been carried out with computational chemist Prof. Jonathan Hirst and co-workers at the University of Nottingham, using quantitative structure-activity relationship (QSAR) models to deduce more information about the PVPi-based polymers in CO_2. It is possible that future work in this area will improve the understanding of the interactions between these stabilisers and CO_2 and lead to further knowledge of the type of stabilisers that should be targeted next.

Further identification of highly CO_2-philic polymers is required for the advancement of commercial application of CO_2 as a medium for dispersion polymerisation, and generating a library of soluble hydrocarbon stabilisers for future use will aid in the realisation of this avenue of research.

6.2.2 Extension to Other Monomer Systems in $scCO_2$

Throughout this thesis, the PVPi-based stabilisers employed in dispersion polymerisation in $scCO_2$ have only found success using the monomer NVP. Attempts to stabilise dispersion polymerisations of monomers such as MMA have proven unsuccessful using the xanthate-capped stabilisers. This observation can be related to the anchor group of the stabiliser. In order for stabilisation to be successful, a stabiliser must possess a reactive or strongly polymer-philic end-group. The xanthate employed in this thesis actively controls monomers such as

N-vinyl pyrrolidone and vinyl acetate, which are vinyl monomers containing an alpha heteroatom. The lack of success with monomers such as MMA is attributed to a poor interaction between the xanthate end-group, which is an unsuitable RAFT agent for MMA, and the growing polymer particles.

Therefore, a crucial requirement for extending the viability of these hydrocarbon stabilisers is to improve their activity in other dispersion polymerisation systems in $scCO_2$. This could involve a number of potential approaches.

One such approach is to employ click chemistry to provide a reactive end-group functionality more suitable for the stabilisation of other monomers.[4-7] Research to this effect is currently being studied within the Howdle group, with as yet unpublished results. Such a method would involve incorporating a terminal group able to act as a CTA for more activated monomers such as MMA (*e.g* dithioester).

Alternatively a 'universal RAFT agent' could provide a solution, and such a RAFT agent has already been reported by Benaglia *et al.*[8] This particular RAFT agent functions by using a 'pH-switch' to shift the activity of the RAFT agent from LAMs (*e.g* VAc) to MAMs (*e.g* MMA). Future efforts could potentially identify a universal RAFT agent suitable for incorporation in hydrocarbon stabilisers and able to function as the reactive end-group in dispersion polymerisation of various monomers in $scCO_2$, through use of a suitable switching mechanism.

Another potential method of developing an MMA-active stabiliser is the incorporation of a strongly polymer-philic anchoring group, which has a high

affinity for the polymer-rich phase. For MMA, this could include a short chain of PMMA attached to the end of the PVAc-*s*-PVPi hydrocarbon stabiliser.

In addition to dispersion polymerisations, it is possible that the PVAc-*b*-PVPi-X stabilisers could find application in emulsion polymerisations utilising water and CO_2. Steric stabilisers are required in these systems to adsorb at the CO_2-aqueous interface. A number of groups have reported successful emulsion polymerisation processes in CO_2 using a range of surfactants, including the use of PVAc-based stabilisers.[9-14] This is an area which could prove interesting to consider further, as these stabilisers appear ideally suited to emulsion polymerisation in CO_2.

Overall, the development of a stabiliser which can be applied to a broad range of polymerisations in $scCO_2$ is crucial if dispersion polymerisations in this medium are to find large-scale application. Also, it is important that synthesis of hydrocarbon stabilisers remains relatively inexpensive and uncomplicated, which can be a problem when faced with additional synthetic transformations. However, further investigation of the stabiliser anchor group and the corresponding effect on dispersion polymerisation of other monomers in $scCO_2$ will undoubtedly lead to solutions to these issues.

6.3 References

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